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WADC TECHNICAL REPORT 59-166

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HEAT CAPACITY DETERMINATION OF MINERAL AND SYNTHETIC ENGINE OILS, LUBRICANTS, FUELS, AND HYDRAULIC FLUIDS IN THE TEMPERATURE RANGE 70°-500°F

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Materials Laboratory
Contract No. AF 33(616)-5269
Project No. 7360
Task No. 73603

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

This report was prepared by Midwest Research Institute under USAF Contract No. AF 33(616)-5269.

The contract was initiated under Project No. 7360, "Materials Analyses and Evaluation Techniques", Task No. 73603, "Thermodynamics and Heat Transfer". It was administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with Mr. Robert A. Winn acting as project engineer.

This report covers work conducted from March 1958 to January 1959.

The work was carried out under the supervision of Dr. John W. Barger, Head, Inorganic Chemistry Section, and Dr. B. W. Beadle, Manager, Chemistry and Chemical Engineering Division. This report was prepared by Mr. Thomas M. Medved, who acted as project leader. Preparation of the experimental design and computations were supervised by Mr. Calvin C. Bolze, Chemical Statistician. The calorimeter was designed by Mr. R. L. Hughes and Dr. J. J. Downs. Mr. C. E. Hansen performed the work and prepared the sections on the Latent Heat of Vaporization of Phenyl Ether Samples. Dr. J. J. Downs designed and built the calorimeter for latent heat of vaporization measurement.

ABSTRACT

The heat capacities of 33 mineral and synthetic engine oils, lubricants, fuels, and hydraulic fluids were measured over a temperature range of 80° to 500°F.

Calorimeter constants were obtained by internal standardization foregoing the use of a standard liquid.

The calculated errors in the final results were 3 to 5 per cent.

A comparison of latent heats of vaporization of phenyl ether samples is included.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

Leo F. Salzberg
Chief, Materials Physics Branch
Materials Laboratory

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PART ONE - HEAT CAPACITY

I. INTRODUCTION

This work is a continuation of the research reported in WADC Technical Report 58-70[1]. New lubricants and hydraulic fluids are being synthesized to meet the increased criteria necessitated by modern engines and missiles. Heat capacity data are necessary for engineering calculations to estimate heat transfer, or thermal diffusivity in bearings or working surfaces.

This report, in conjunction with WADC Technical Report 58-70, describes a unique, simple, and rapid method for measuring and calculating heat capacities over an extended temperature range.

II. SUMMARY AND CONCLUSIONS

Adiabatic calorimeters were developed which facilitated the measurement of the heat capacity of liquid materials stable in the 70° to 500°F temperature range. The calorimeters were designed and constructed of glass so that the sample liquid was contained in a Dewar type flask. Mercury was admitted to the Dewar jacket to rapidly establish temperature equilibrium between the sample and thermostat. Upon reaching equilibrium, the mercury was removed and the Dewar flask evacuated through a trap immersed in liquid nitrogen. This rendered the calorimeter nearly adiabatic.

The method of calculation used the heat loss rates before and after the heating cycle and the heat gain rate during the heating cycle. The rate of energy input to the sample and calorimeter was determined by the electrical potential and current.

The heat capacities of 33 lubricants and hydraulic fluids were measured at 80°, 185°, 290°, 395° and 500°F, if they were liquid and stable at these temperatures. Duplicate runs were made using two sample sizes, namely, 75 and 150 ml. This enabled calorimeter constants to be obtained without the use of a calibrating standard.

Manuscript released by the authors 26 February 1959 for publication as a WADC Technical Report.

The least squares method was used to calculate the "best-fit" linear relationship between heat capacity and temperature for each of the oils in the temperature range of 70° to 500°F. The error calculated for these measurements ranged from 3 per cent to 5 per cent.

III. DISCUSSION AND RESULTS

Each oil sample was run in duplicate, using 75 ml. in one calorimeter and 150 ml. in a different calorimeter. Four measurements were made on each of these samples, giving a total of eight values at each temperature point. The temperature points were 80°, 185°, 290°, 395° and 500°F.

The order of measurement in respect to temperature (290°, 500°, 80°, 185° and 395°F) was established to minimize errors resulting from changes in the oils. If any loss occurred after the 500°F measurement a fresh charge was put into the calorimeter so that measurements at 80°, 185° and 395°F would not be affected by this loss. The 500°F values in this case were not used in any calculations of heat capacity.

The oils that exhibited thermal instability were: LRO-1, LRO-2, LRO-4, MLO-58-586 and MLO-58-587. MLO-58-658 was not measured at 395° and 500°F on WADC instructions. Oil O-57-3U solidified at 500°F, and formed large amounts of sludge at other temperatures; consequently, the data on this oil are aberrant.

Low temperature data were not obtained on several oils, because they are solids at these temperatures. At 80°F MLO-58-418, MLO-58-432, MLO-58-588, MLO-58-589, MLO-58-590 and MLO-58-591 are solids. At 185°F MLO-58-432, MLO-58-590 and MLO-58-591 are solids.

The experimental design was based on the assumption that the new oils would be comparable to those reported in WADC TR 58-70 and that heat capacity values would be attainable at each of the five temperatures. Unfortunately, this was not so because only 18 of the 33 oils had measurable specific heats at all five points. As a consequence only these oils could be used in calculating calorimeter constants and these values are therefore less precise than originally intended. Statistical analysis of the data showed that the observed calorimeter differences are within the experimental error. Furthermore, corrections are adequately represented by a linear function of temperature as given in Table I.

TABLE I

CALORIMETER CONSTANTS

Constant, Btu/°F				
80°F	185°F	290°F	395°F	500°F
11.19	11.82	12.44	13.07	13.70

The values of the measured heat capacities are shown in Table II. These values are computed by adding the data of the 75-ml. and 150-ml. runs, giving a total weight based on 225 ml. of sample. The first 16 oils listed were used in the computation of calorimeter constants.

TABLE II

HEAT CAPACITY, BTU/LB/°F

Sample	80°F	185°F	290°F	395°F	500°F
MLO-56-200	0.418	0.500	0.596	0.624	0.766
MLO-57-628	0.511	0.595	0.655	0.785	0.840
MLO-58-342	0.440	0.500	0.547	0.612	0.725
O-56-36N	0.479	0.567	0.608	0.695	0.731
O-56-36U	0.481	0.538	0.584	0.615	0.669
O-56-57N	0.471	0 532	0.585	0.639	0.711
O-56-57U	0.458	0.539	0.575	0.716	0.742
O-57-13	0.453	0.523	0.556	0.572	0.612
O-57-36	0.405	0.493	0.534	0.692	0.785
O-58-6	0.365	0.403	0.433	0.484	0.487
O-58-8	0.269	0.352	0.358	0.401	0.430
O-58-12	0.476	0.544	0.617	0.674	0.668
O-58-13	0.482	0.582	0.595	0.645	0.651
LRO-3	0.162	0.231	0.259	0.266	0.306
Richfield L8-32	0.481	0.484	0.594	0.637	0.636
Cal Research Fluid 341	0.456	0.502	0.544	0.644	0.647
MLO-58-418	-	0.454	0.460	0.639	0.535
MLO-58-432	-	-	0.471	0.538	0.575
MLO-58-586	0.406	0.469	0.487	0.532	-
MLO-58-587	0.410	0.434	0.510	0.615	-
MLO-58-588	-	0.426	0.456	0.495	0.553
MLO-58-589	-	0.461	0.471	0.498	0.499

TABLE II (Concluded)

HEAT CAPACITY, BTU/LB/°F

Sample	80°F	185°F	290°F	395°F	500°F
MLO-58-590	-	-	0.462	0.482	0.542
MLO-58-591	-	-	0.473	0.546	0.584
MLO-58-654	0.414	0.539	0.590	0.731	0.686
MLO-58-658	0.369	0.425	0.450	-	-
O-56-3N	0.475	0.531	0.621	0.727	0.684
O-57-3U	0.286	0.447	0.566	1.050	0.619
O-57-19	0.361	0.422	0.414	0.540	-
O-57-37	0.428	0.539	0.566	0.626	-
LRO-1	0.242	0.285	0.276	0.276	-
LRO-2	0.240	0.269	0.276	0.277	-
LRO-4	0.230	0.316	0.268	0.294	-

The data contained in Table II were used in preparing the graphs shown as Figs. 1 through 33, inclusive. The lines were calculated by the least squares method and the equations relating heat capacity and temperature are shown for each oil.

The errors found for the least squares values are shown in Table III. These values apply to samples with a density of 1.0 gm/ml. The correct standard error for a sample is the tabulated value divided by the sample density.

TABLE III

CALCULATED HEAT CAPACITY ERRORS
(Btu/Lb/°F)

Temperature	Standard Error	95% Confidence Limits
80°F	0.024	0.048
185°F	0.017	0.034
290°F	0.014	0.027
395°F	0.017	0.034
500°F	0.024	0.048

No attempt was made to calculate the least squares line for O-57-3U because of its unstable nature.

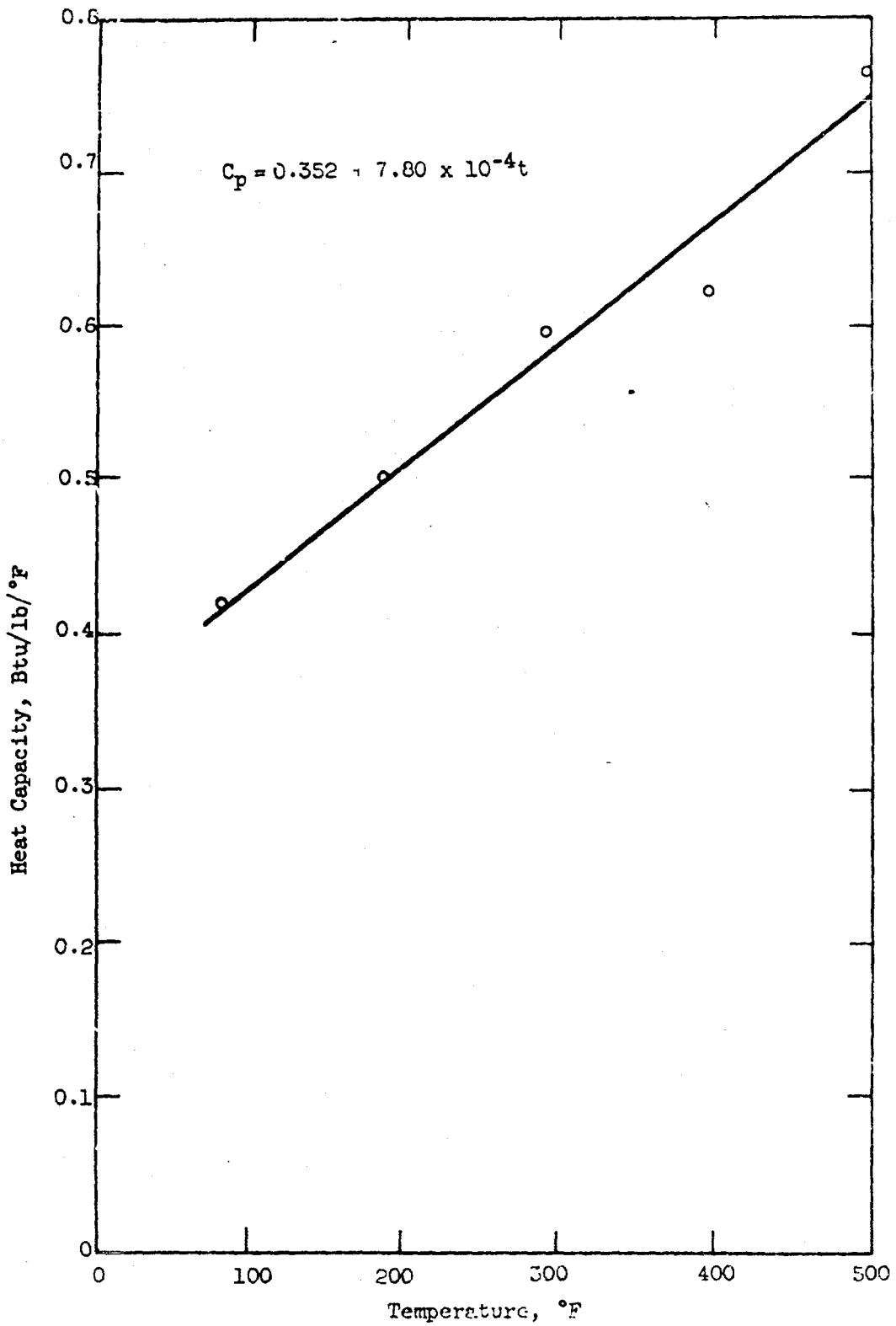

Fig. 1 - Heat Capacity of ML0-56-200

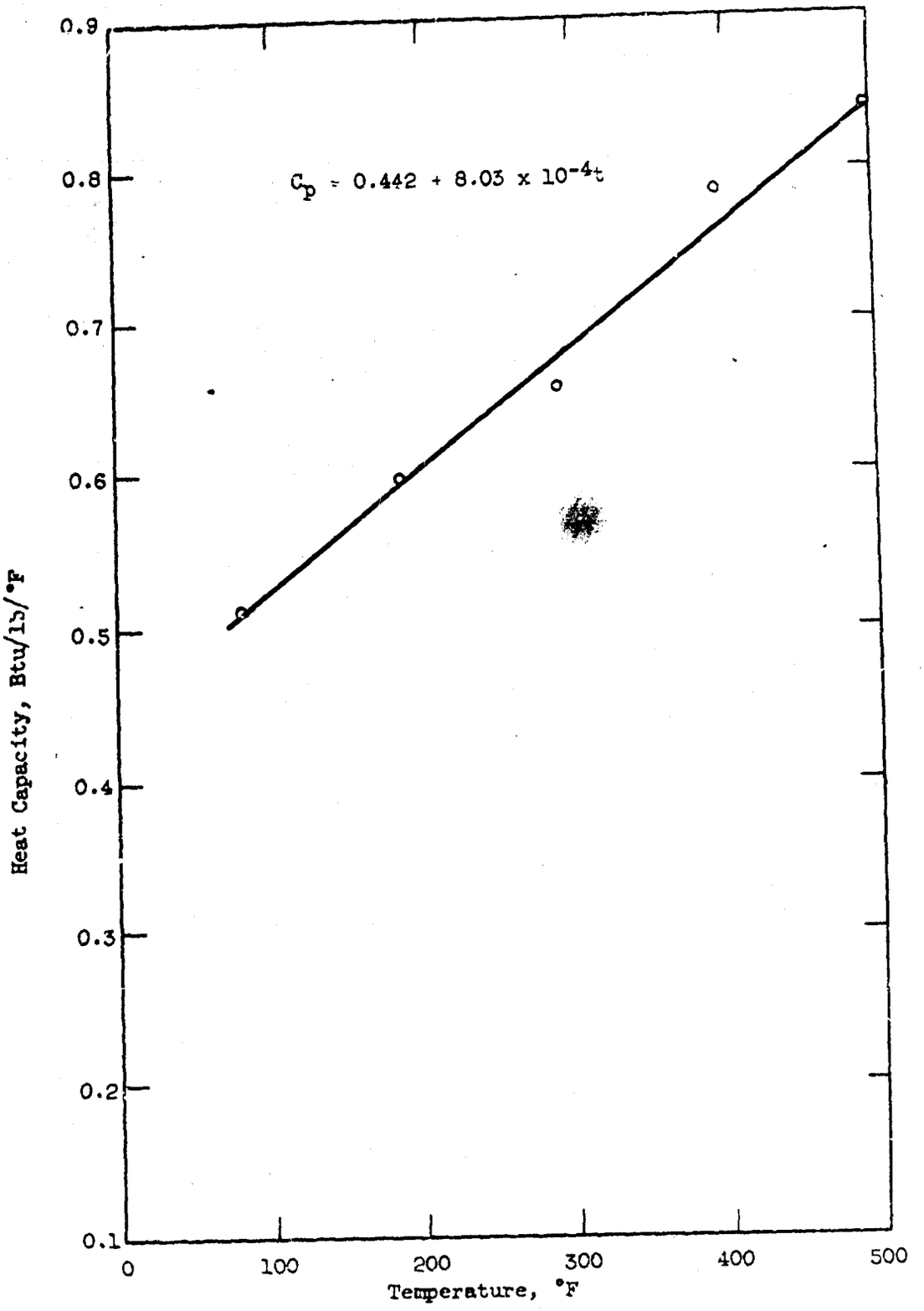

Fig. 2 - Heat Capacity of MLO-57-628

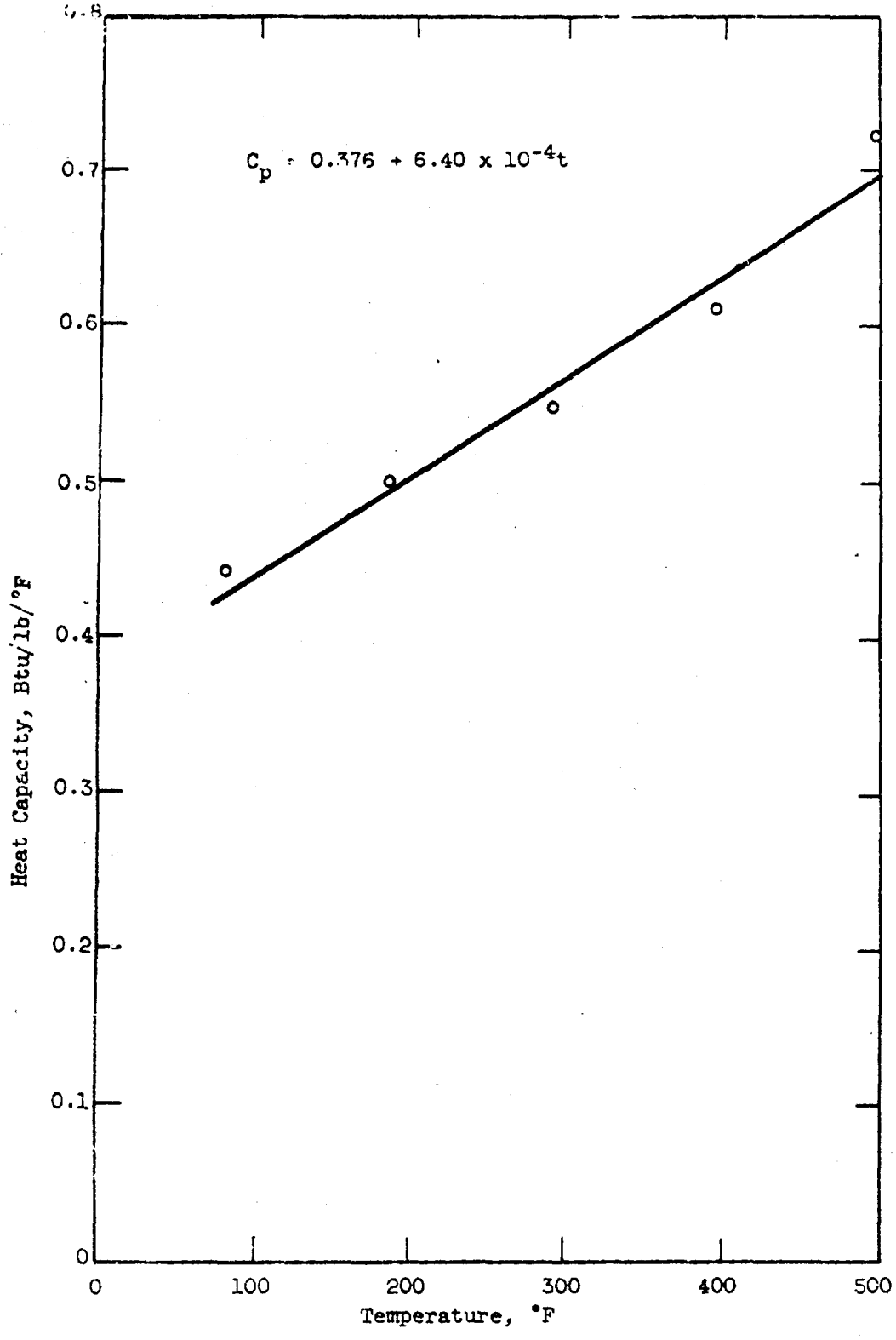

Fig. 3 - Heat Capacity of MLO-58-342

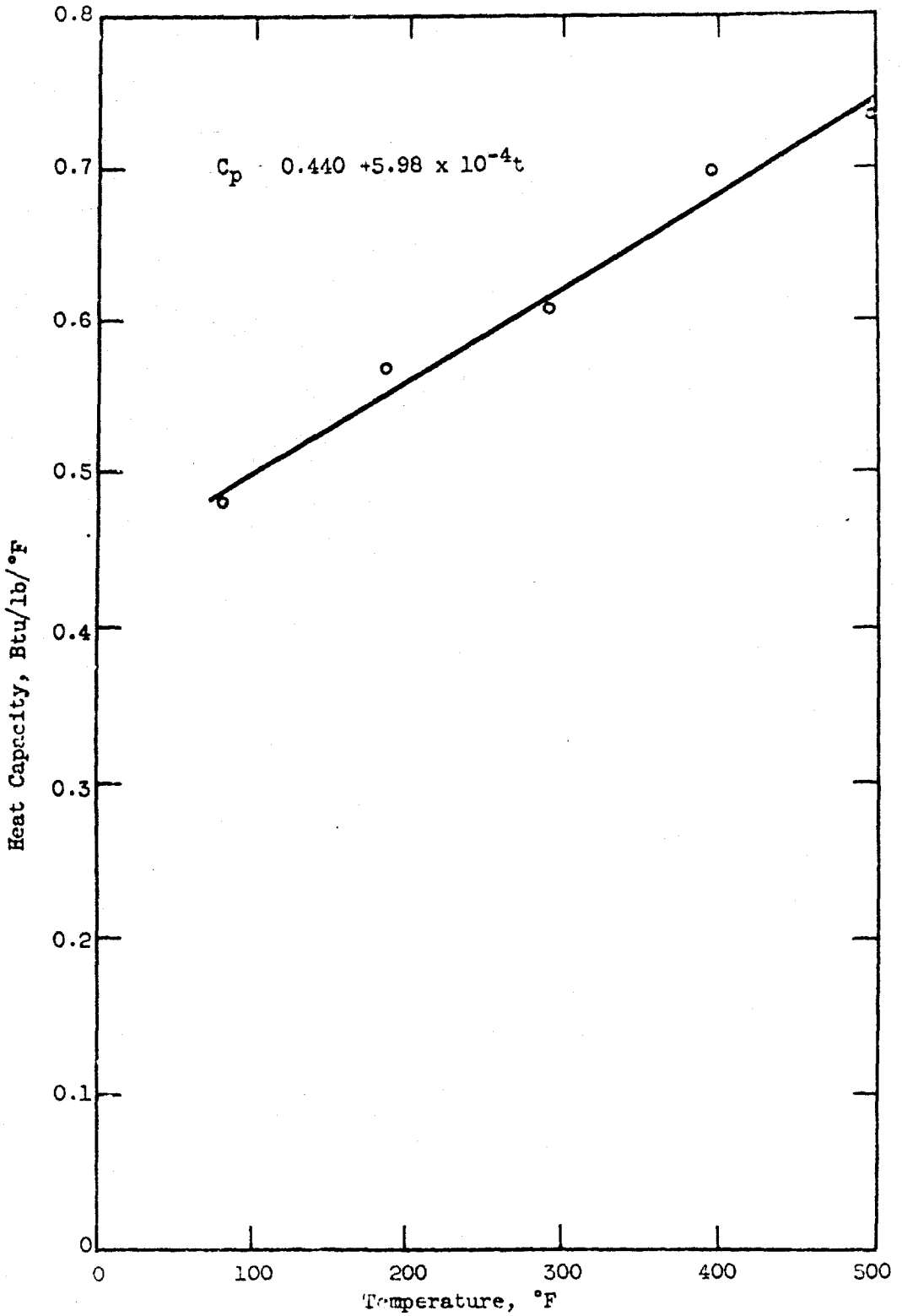

Fig. 4 - Heat Capacity of O-56-36N

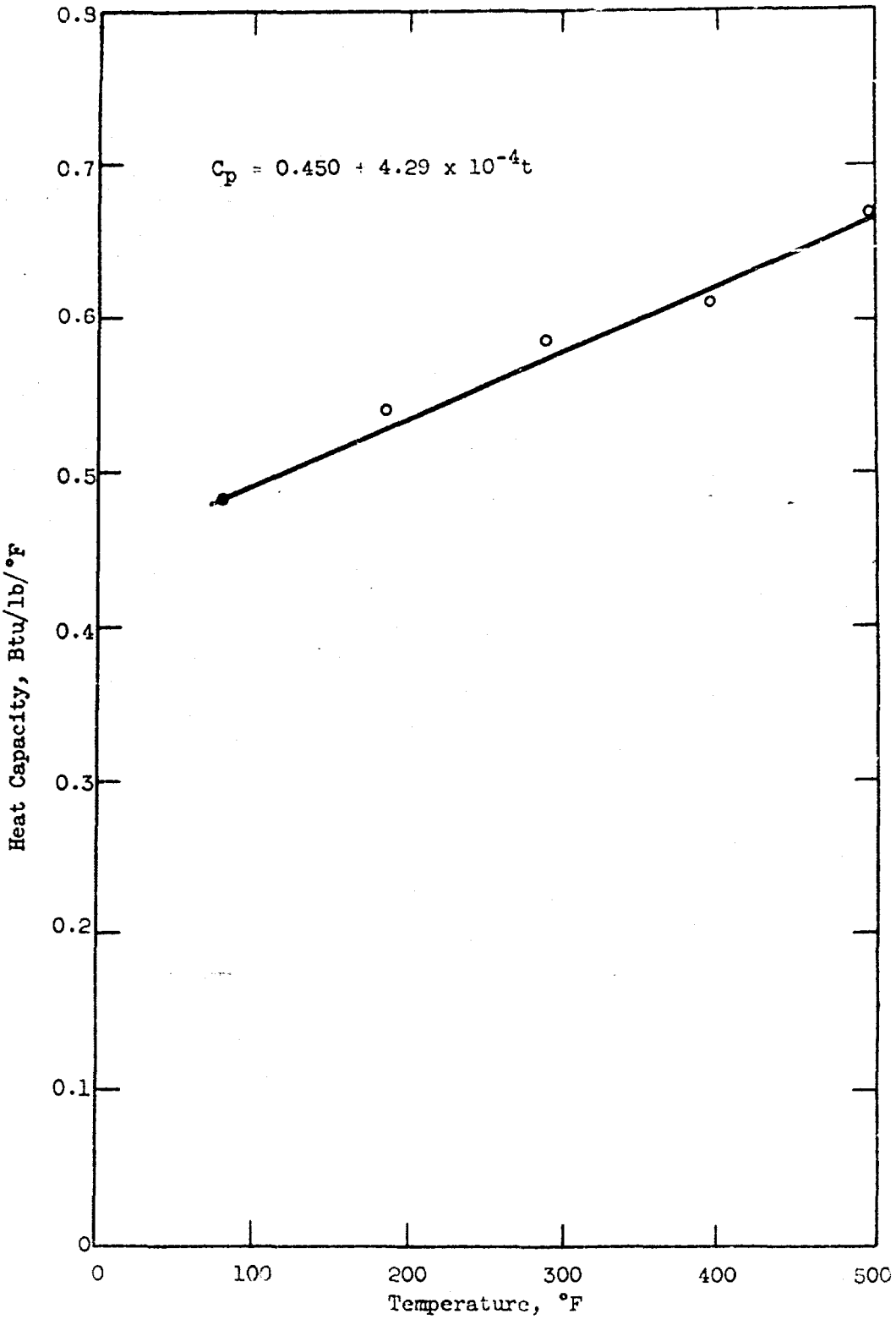

Fig. 5 - Heat Capacity of O-56-36U

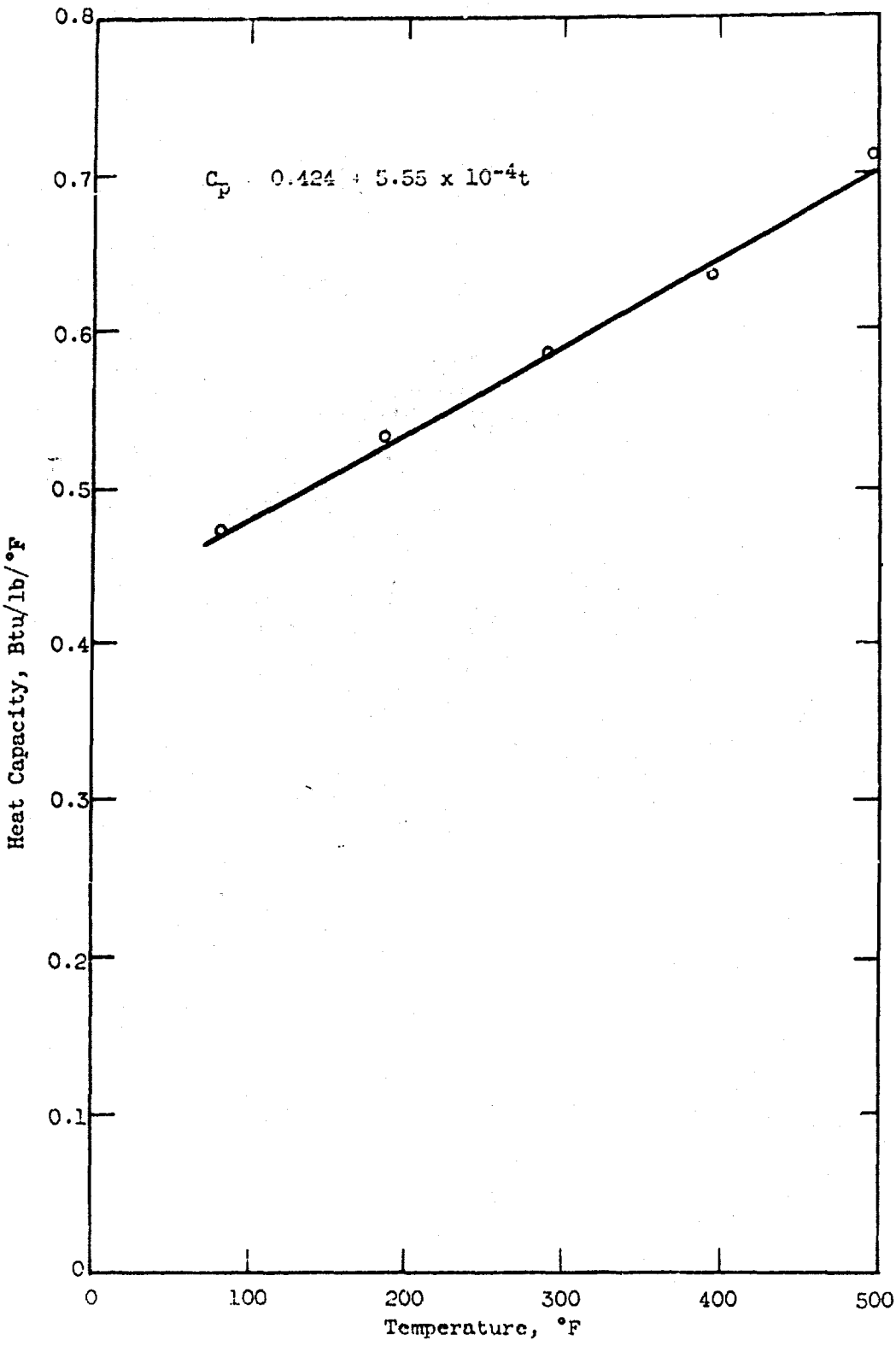

Fig. 6 - Heat Capacity of O-56-57N

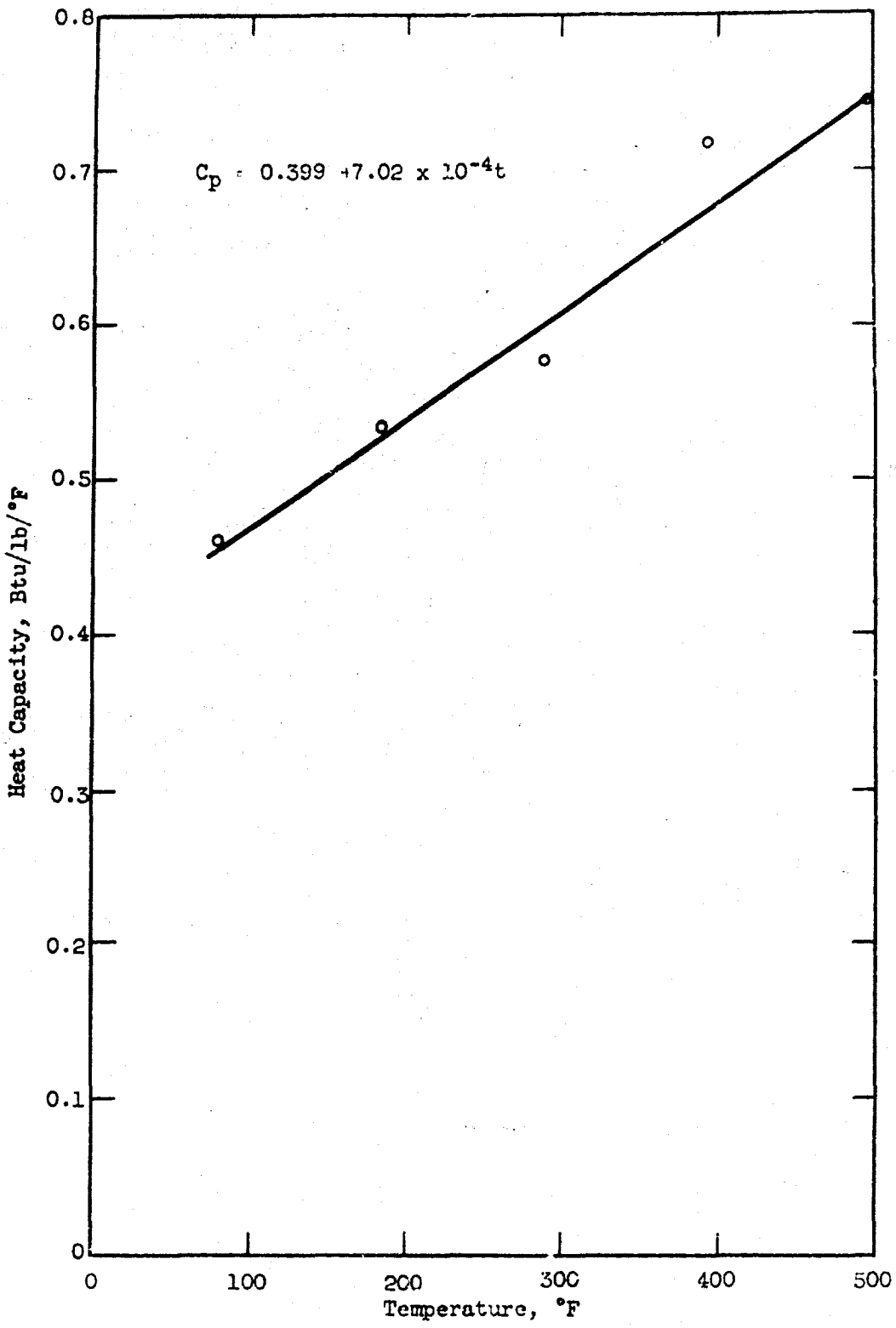

Fig. 7 - Heat Capacity of O-56-57U

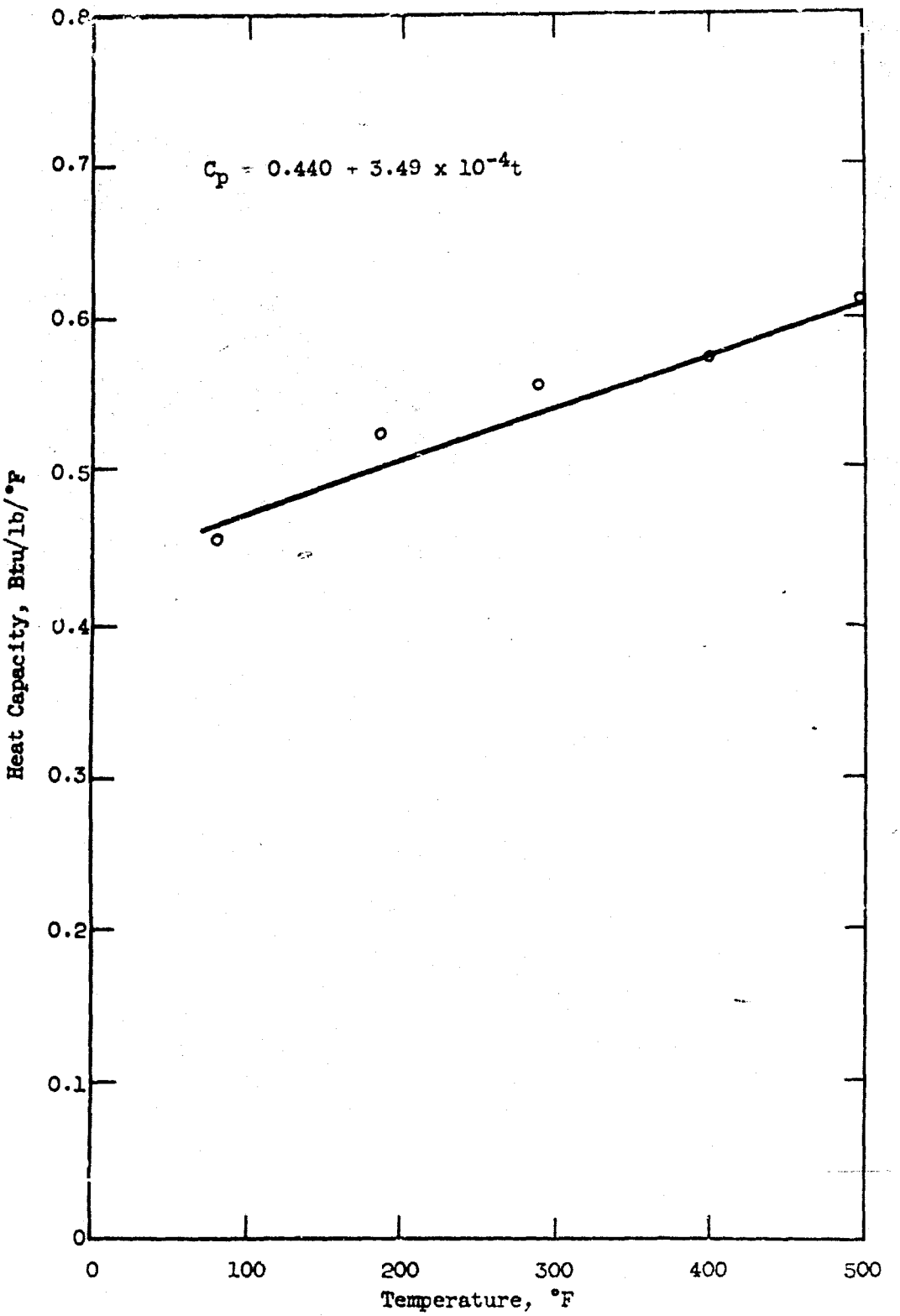

Fig. 8 - Heat Capacity of 0-57-13

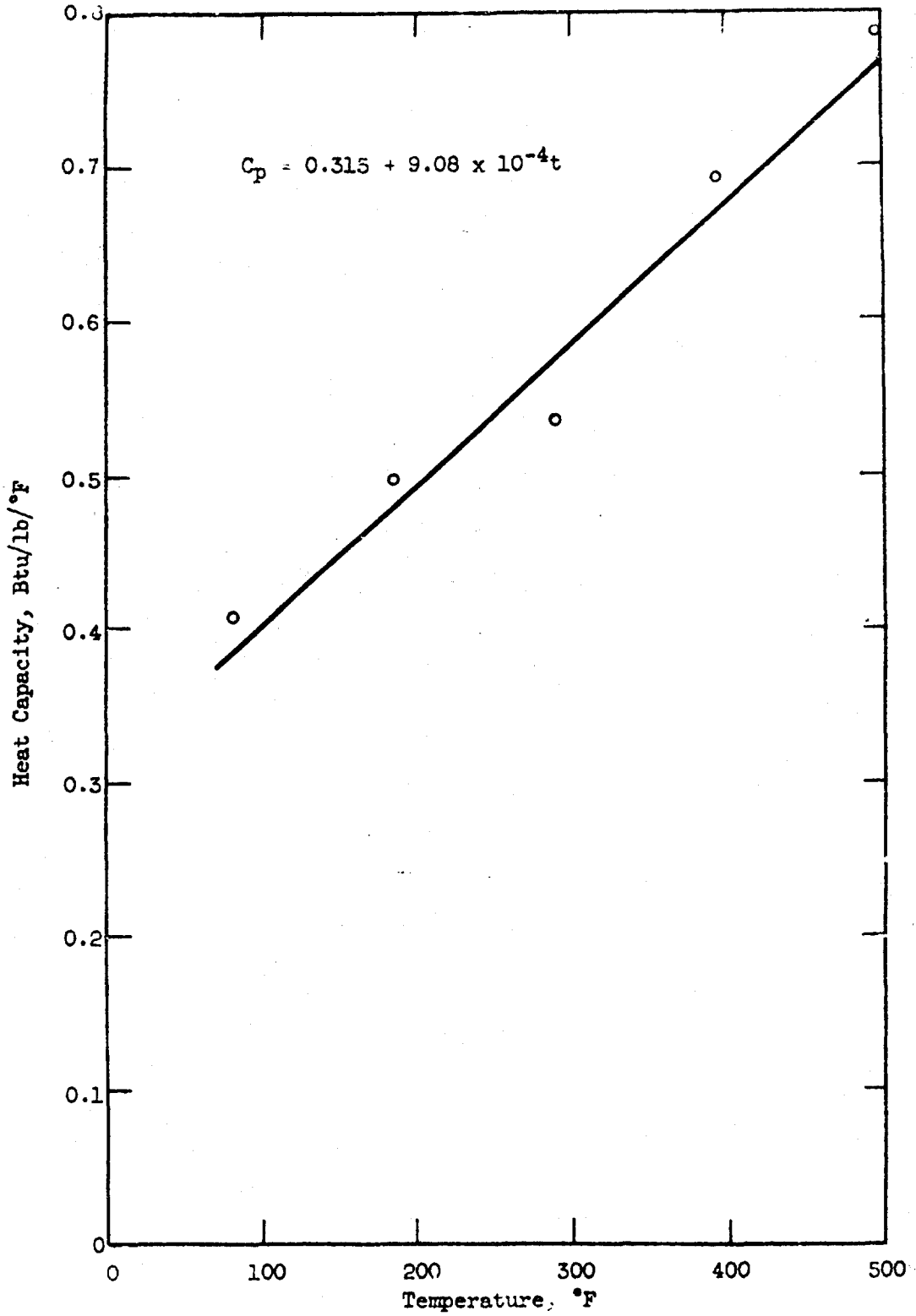

Fig. 9 - Heat Capacity of 0-57-36

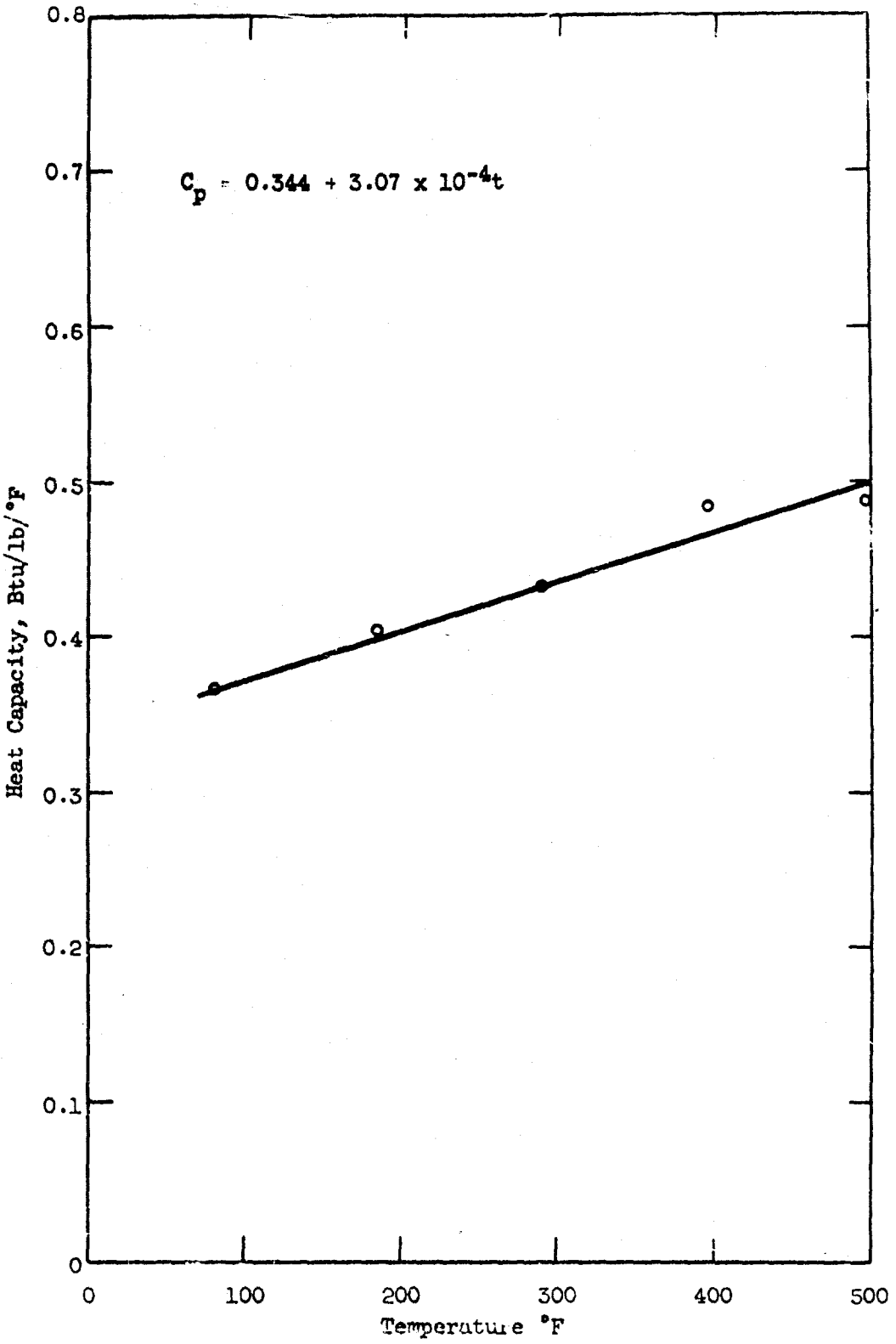

Fig. 10 - Heat Capacity of 0-58-6

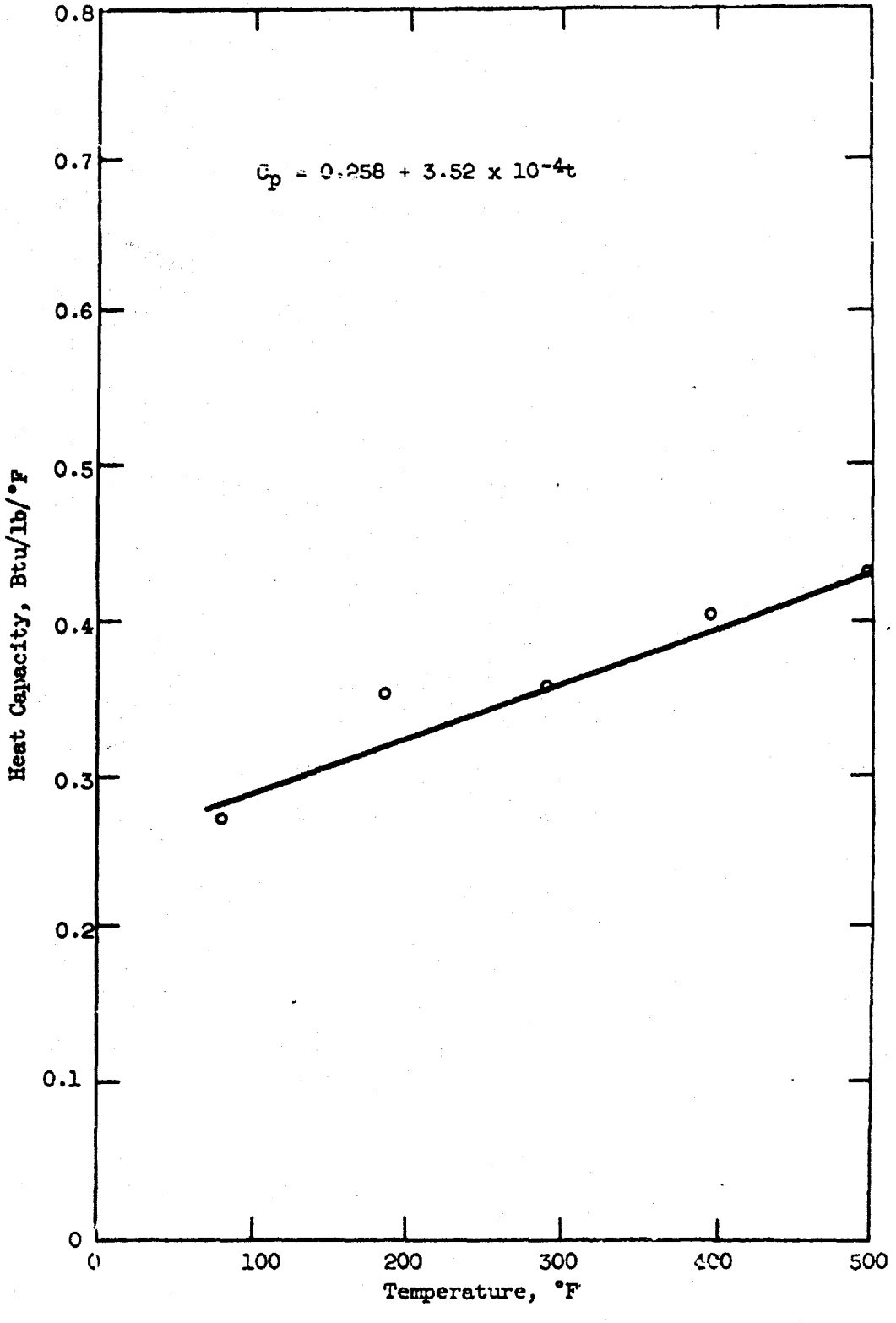

Fig 11 - Heat Capacity of 0-58-8

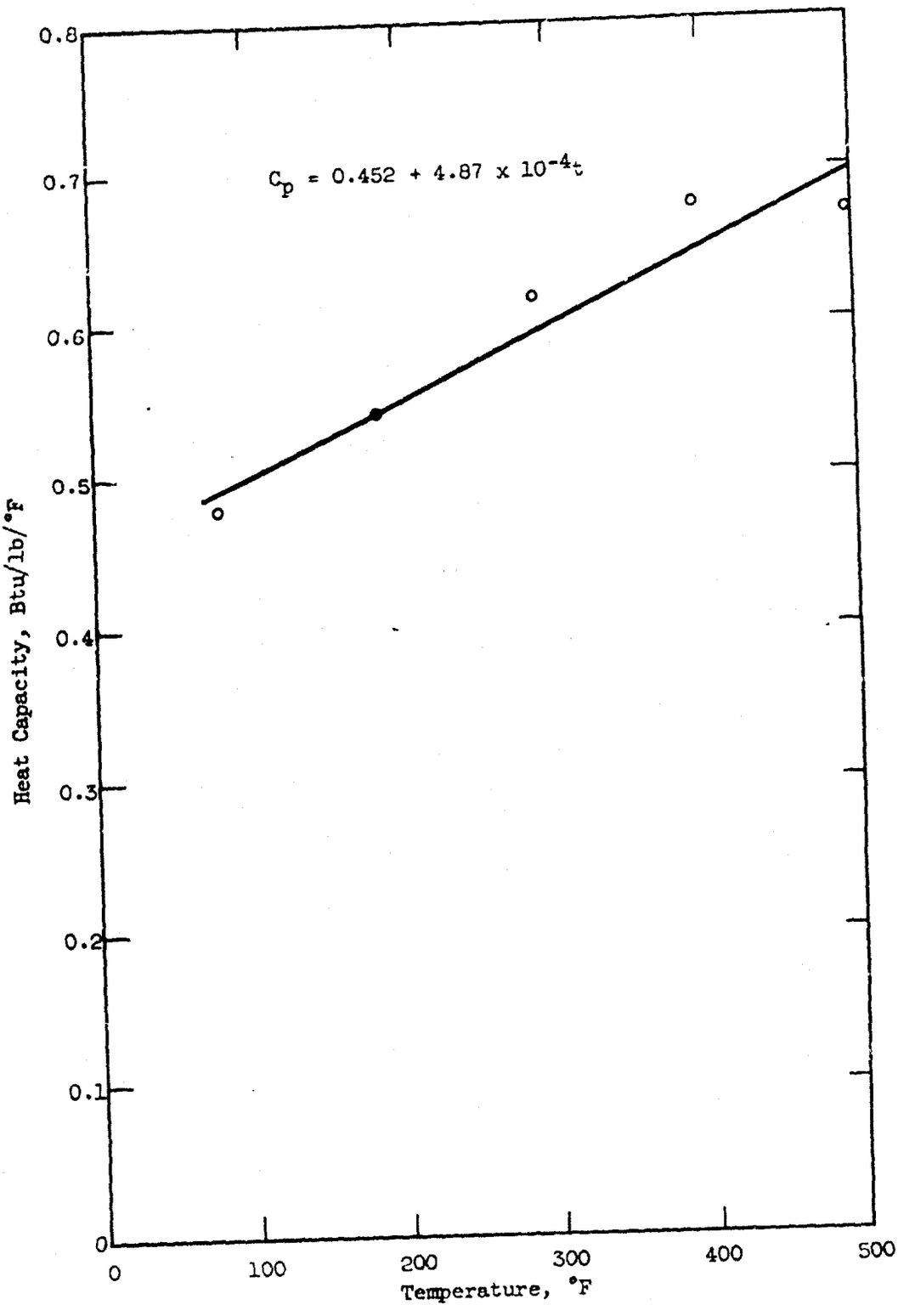

Fig. 12 - Heat Capacity of 0-58-12

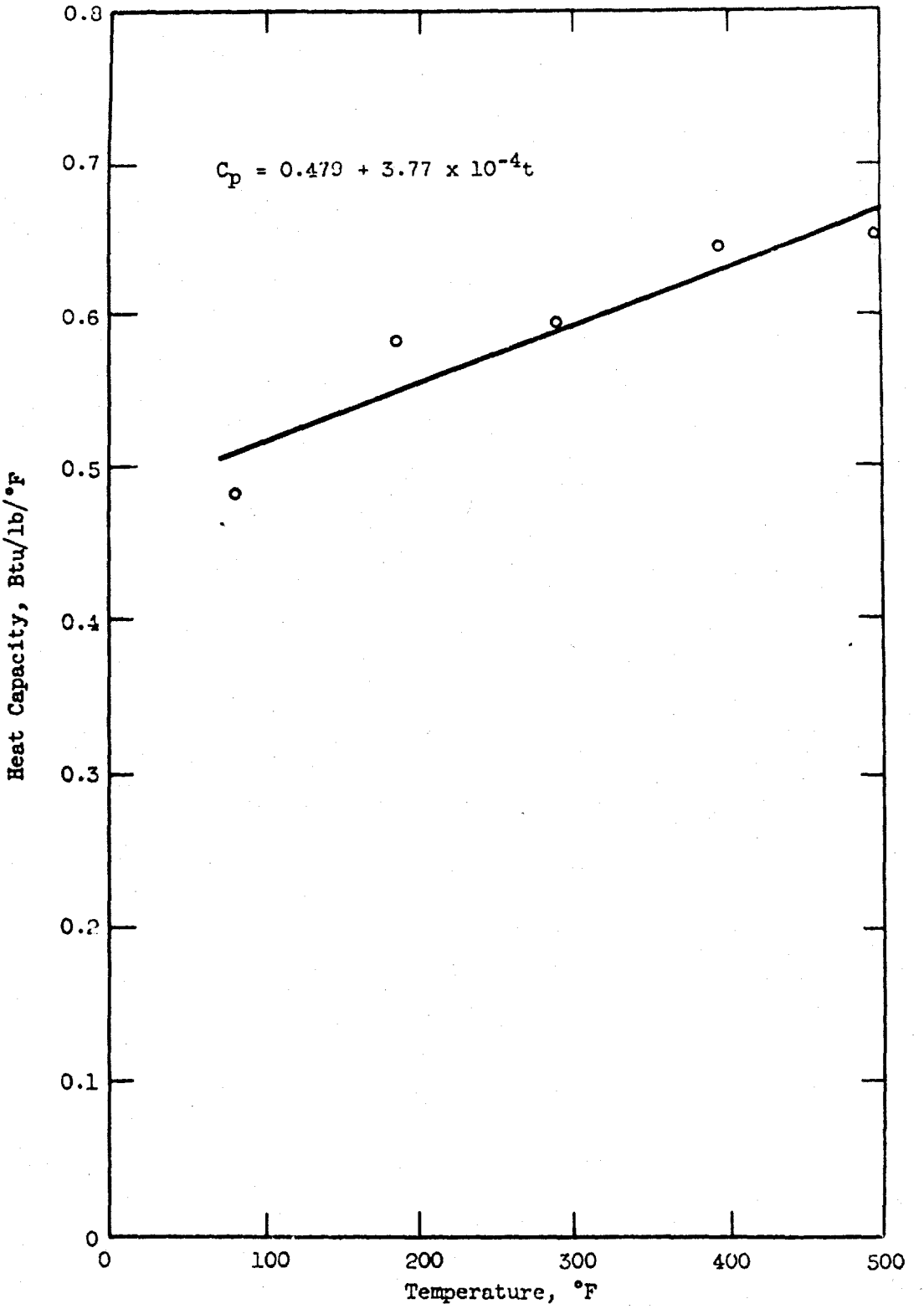

Fig. 13 - Heat Capacity of O-58-13

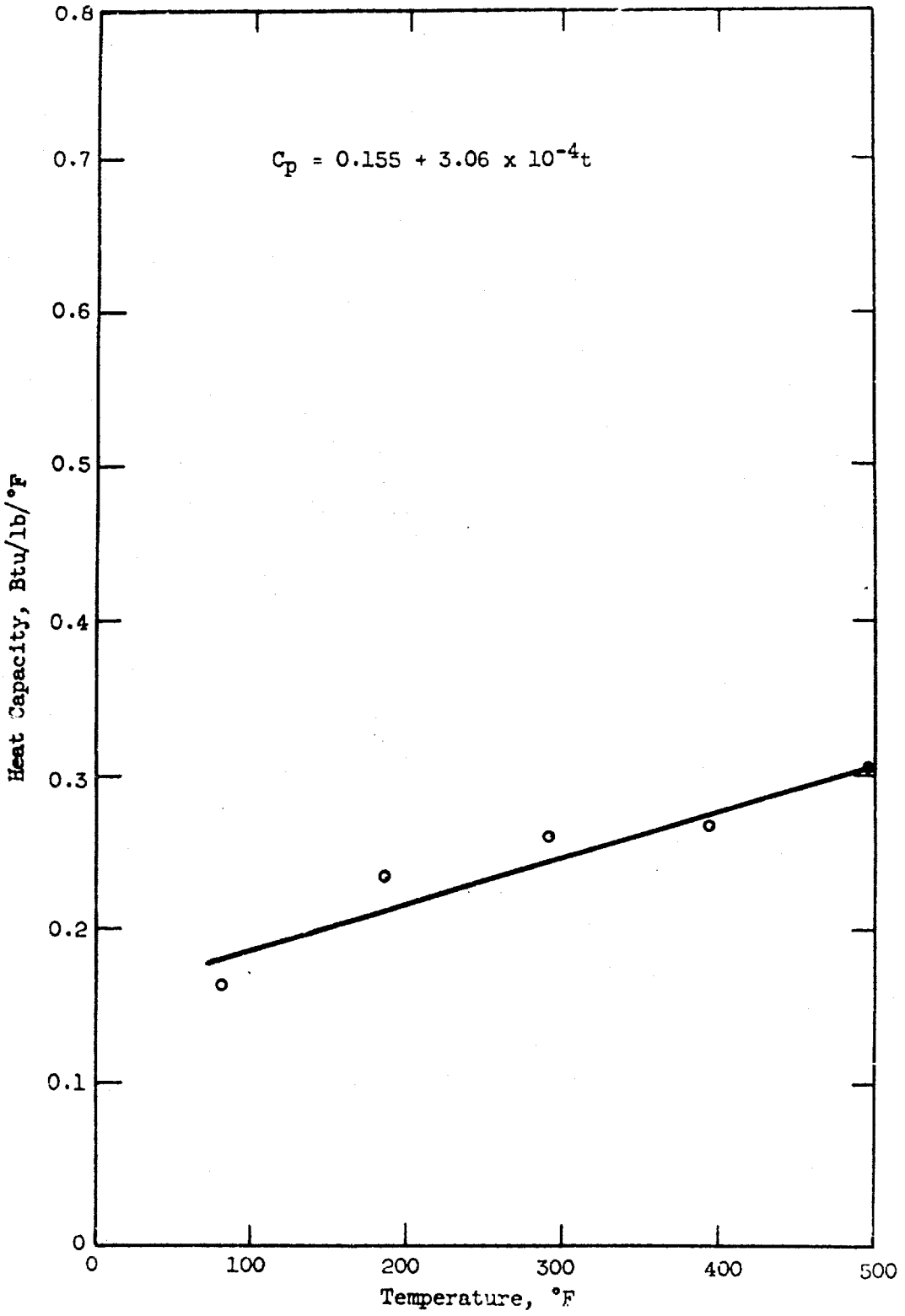

Fig. 14 - Heat Capacity of LRO-3

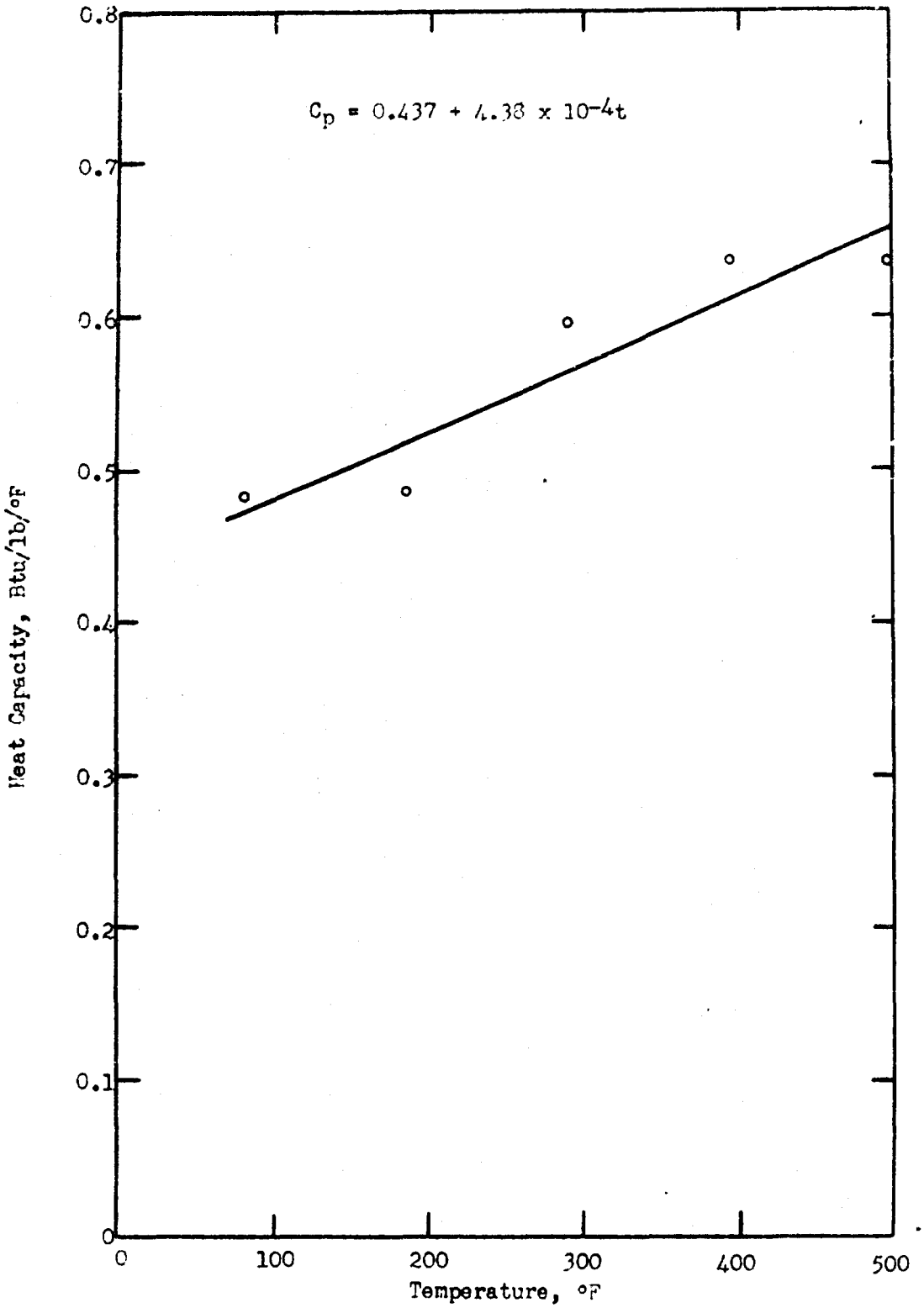

Fig. 15 - Heat Capacity of Richfield 18-32

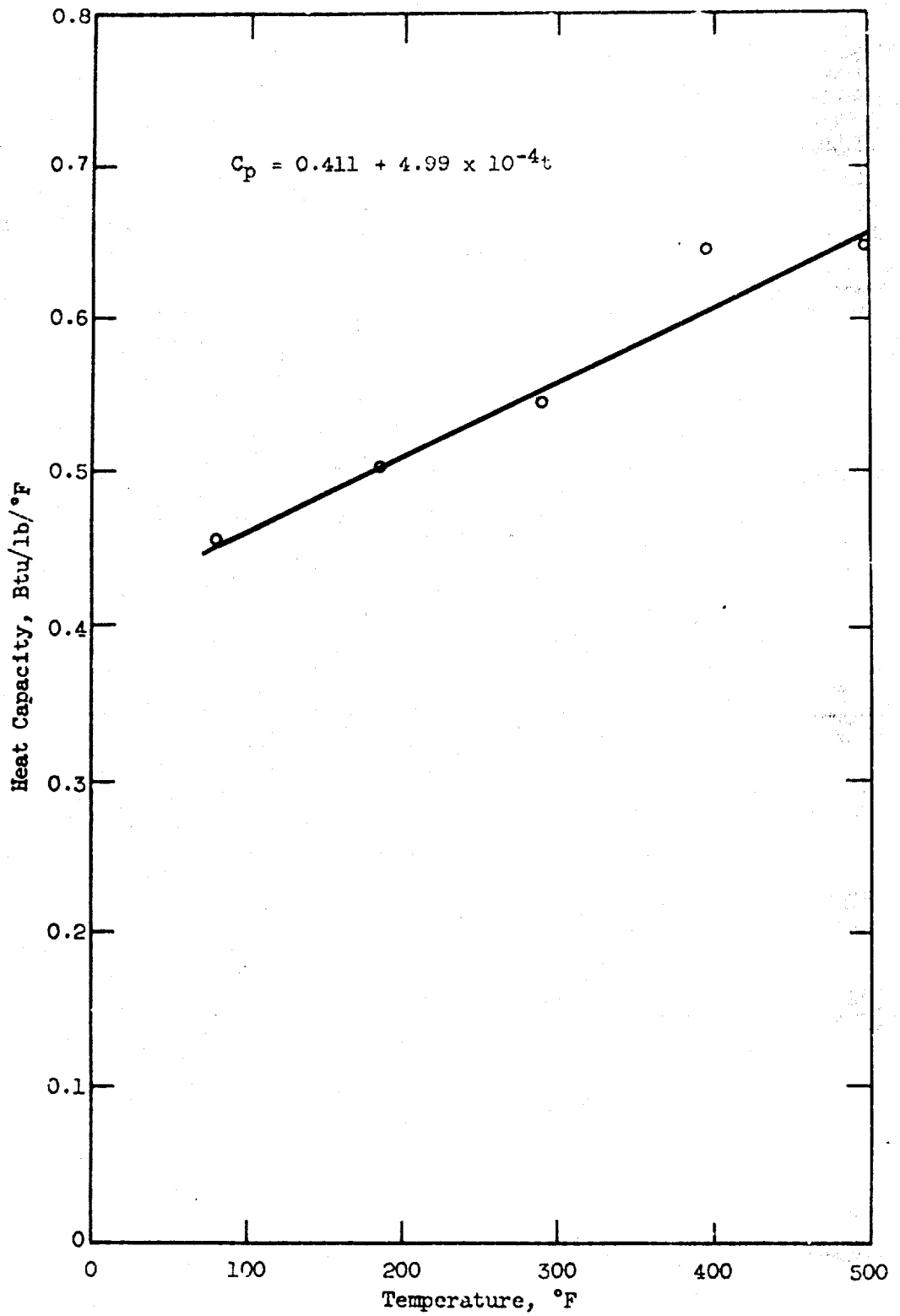

Fig. 16 - Heat Capacity of Cal Research Fluid 341

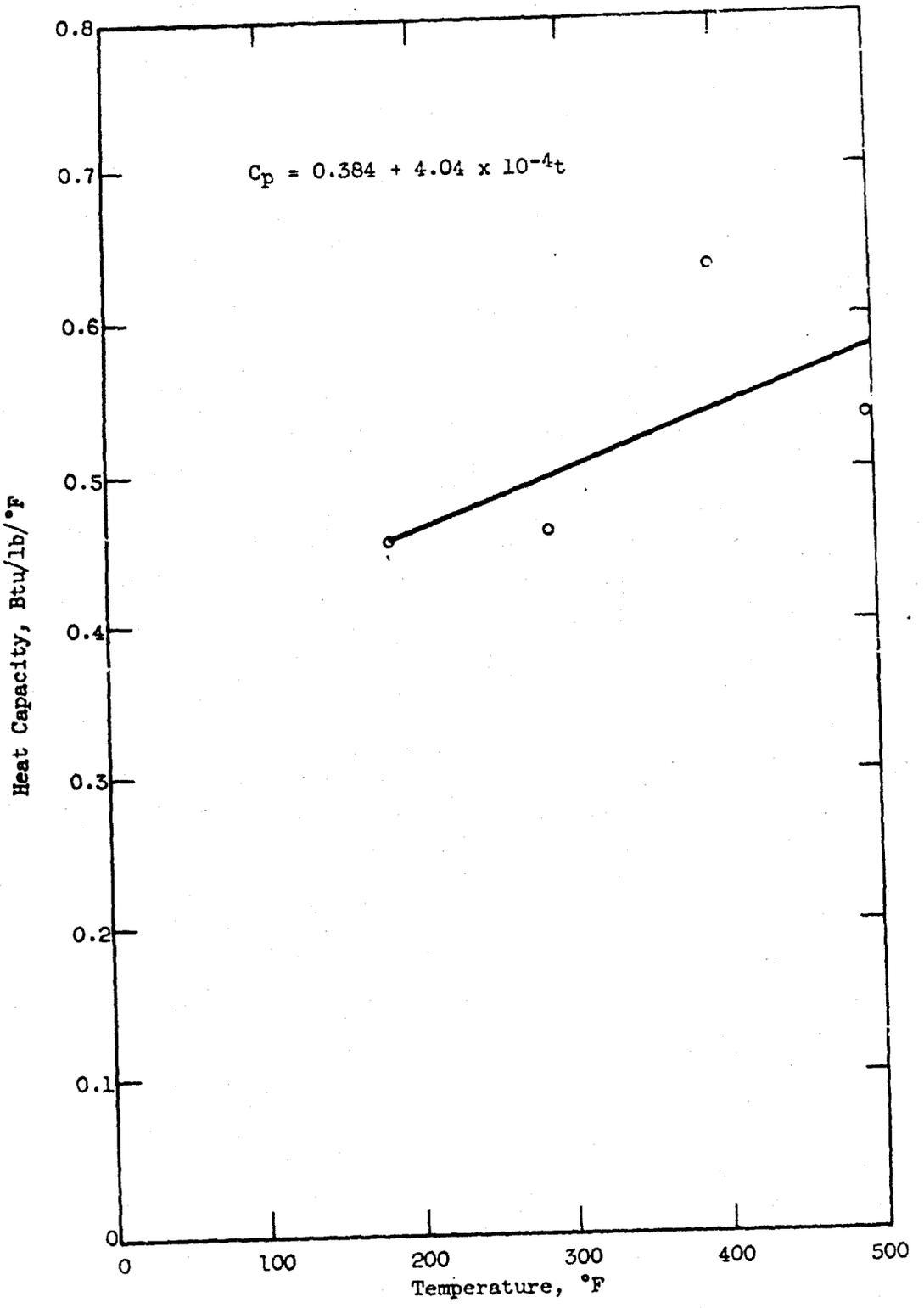

Fig. 17 - Heat Capacity of MLO-58-418

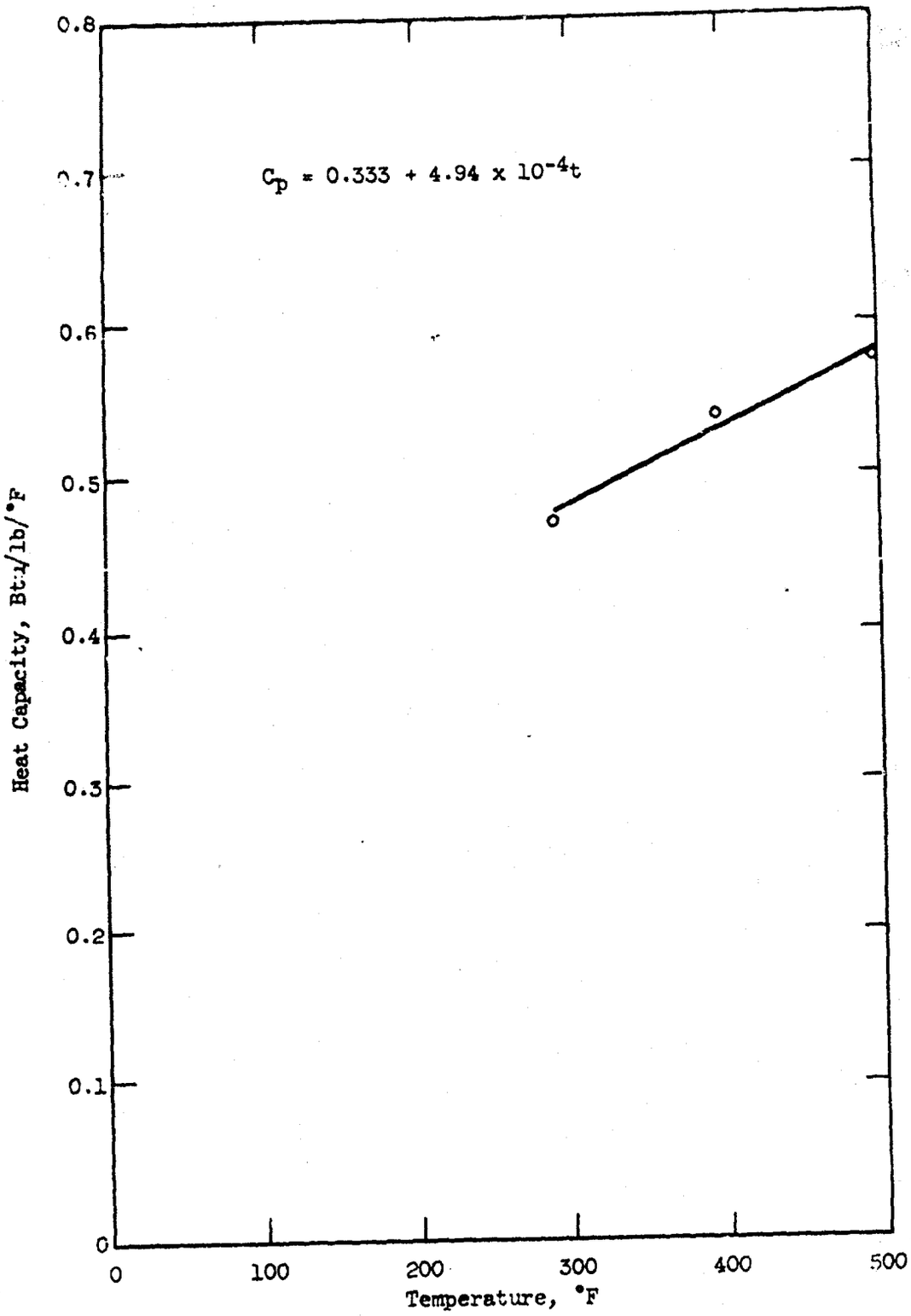

Fig. 18 - Heat Capacity of MLO-58-432

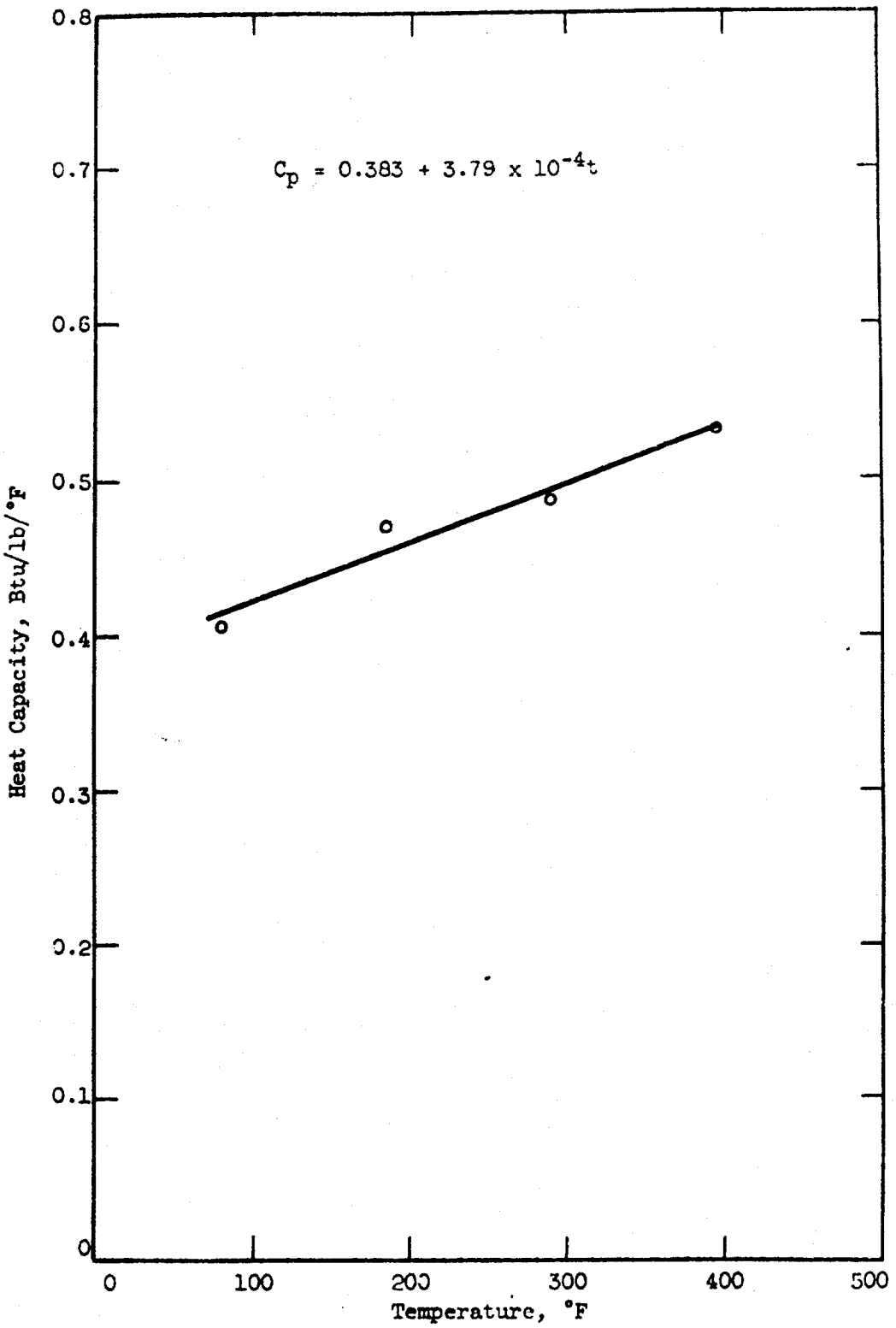

Fig. 19 - Heat Capacity of MLO-58-586

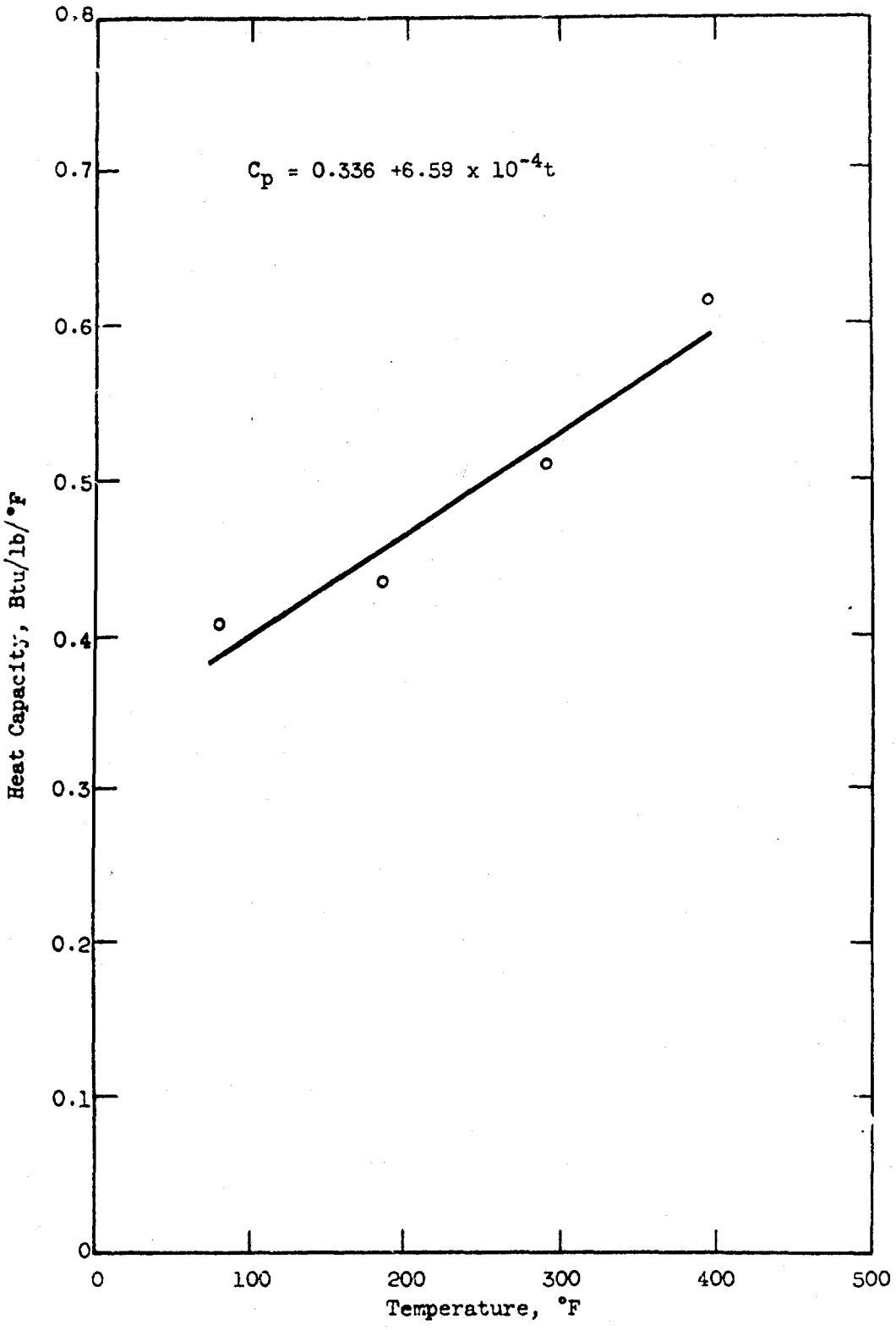

Fig. 20 - Heat Capacity of MLO-58-587

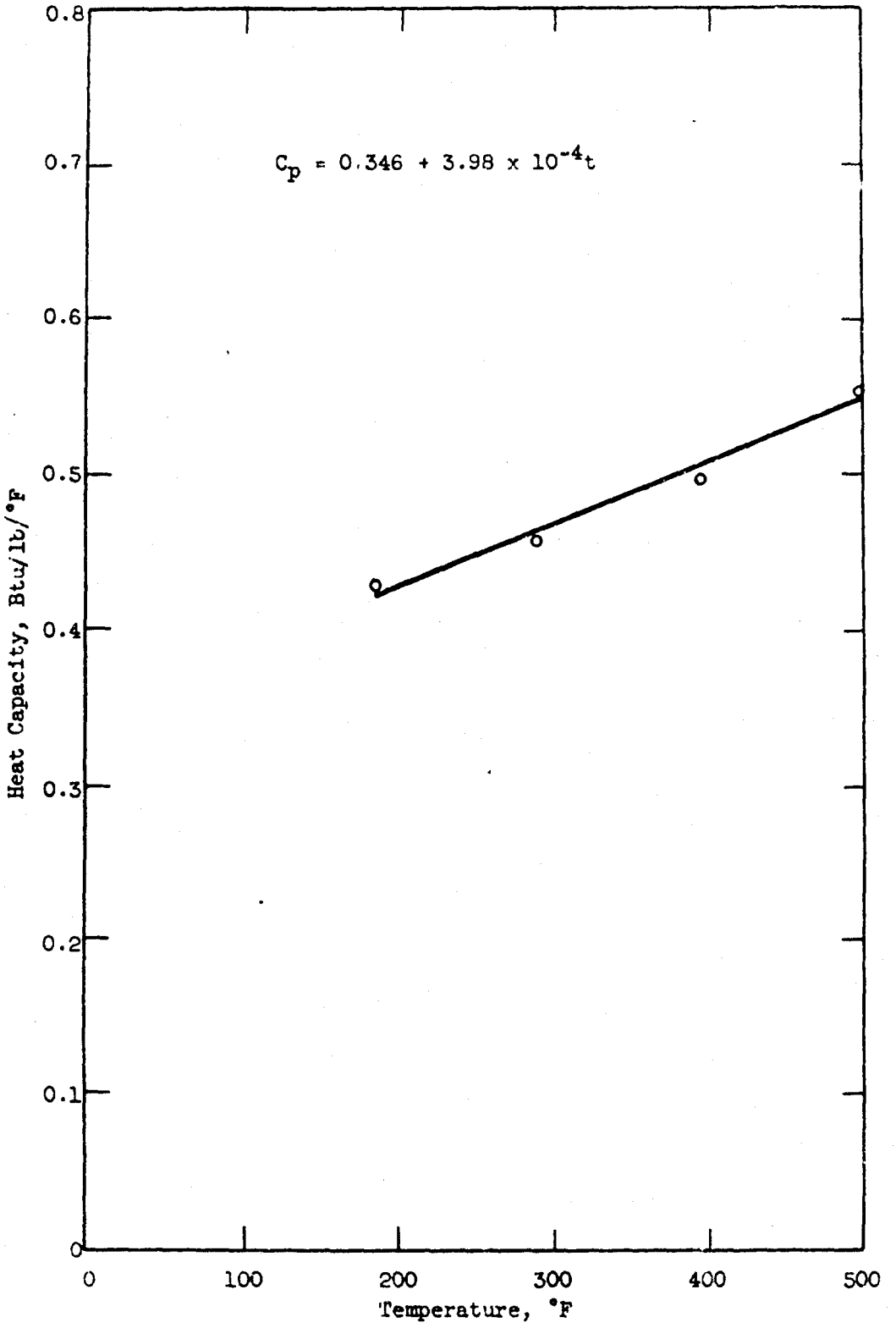

Fig. 21 - Heat Capacity of MLO-58-588

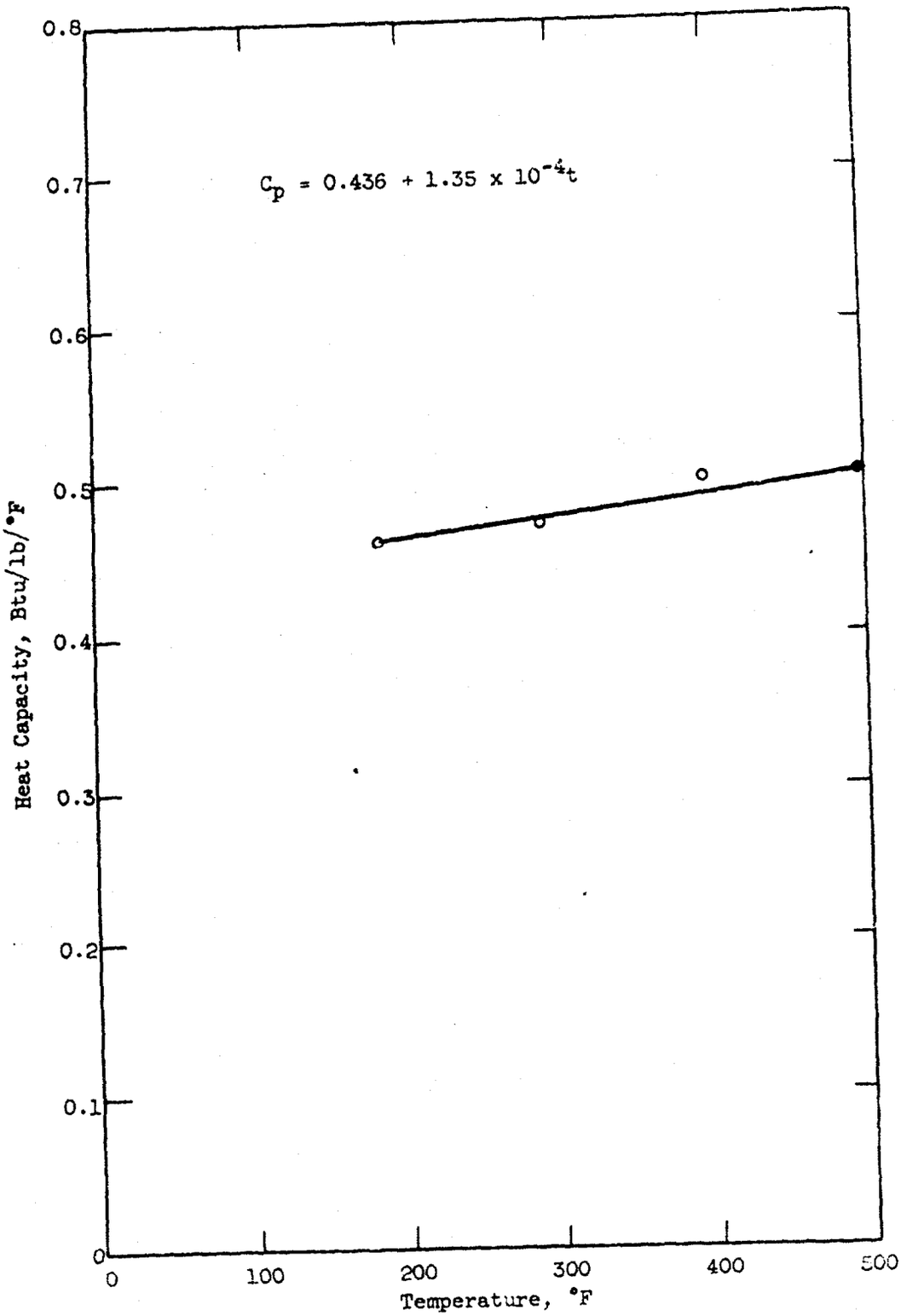

Fig. 22 - Heat Capacity of ML0-58-589

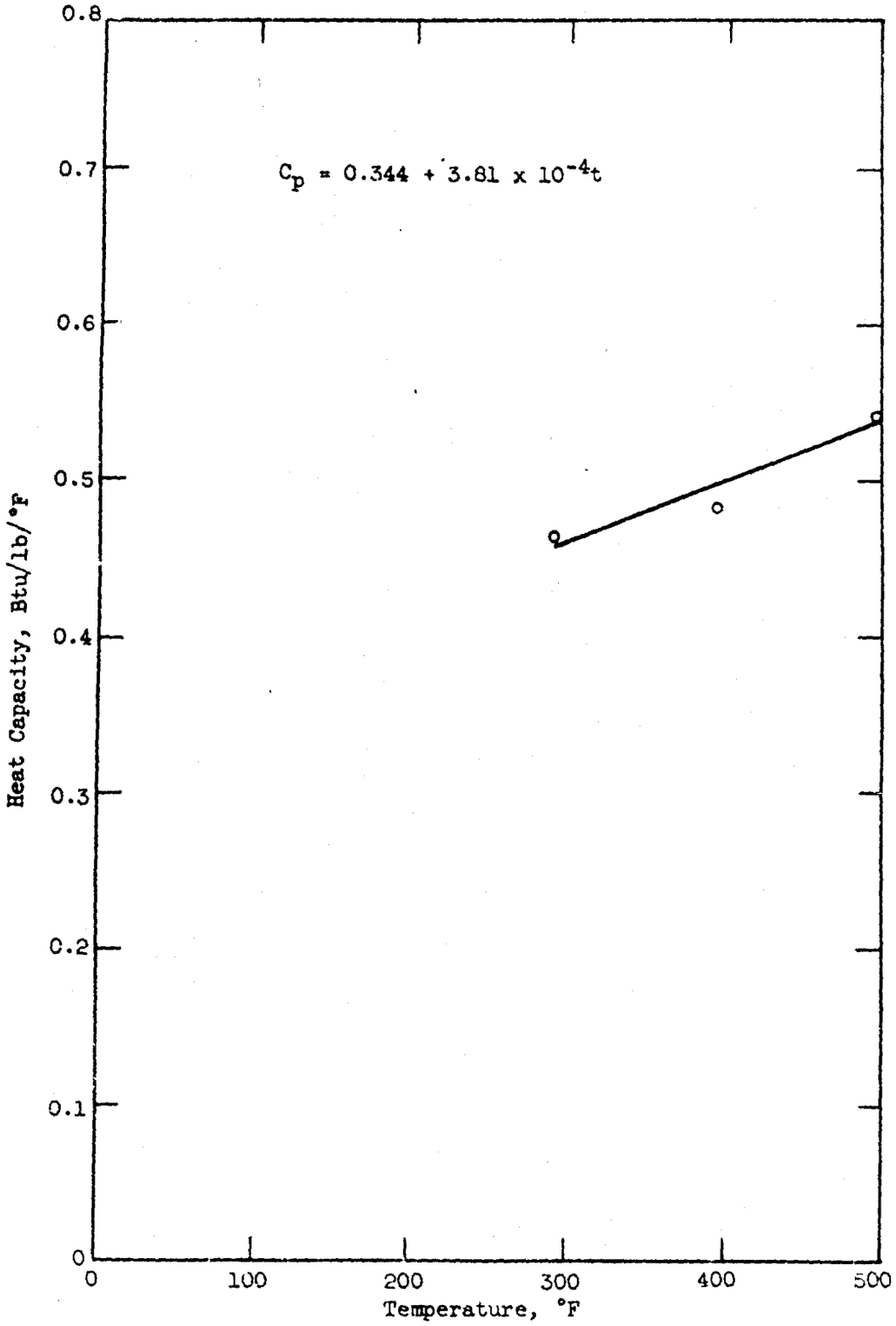

Fig. 23 - Heat Capacity of MLC-58-590

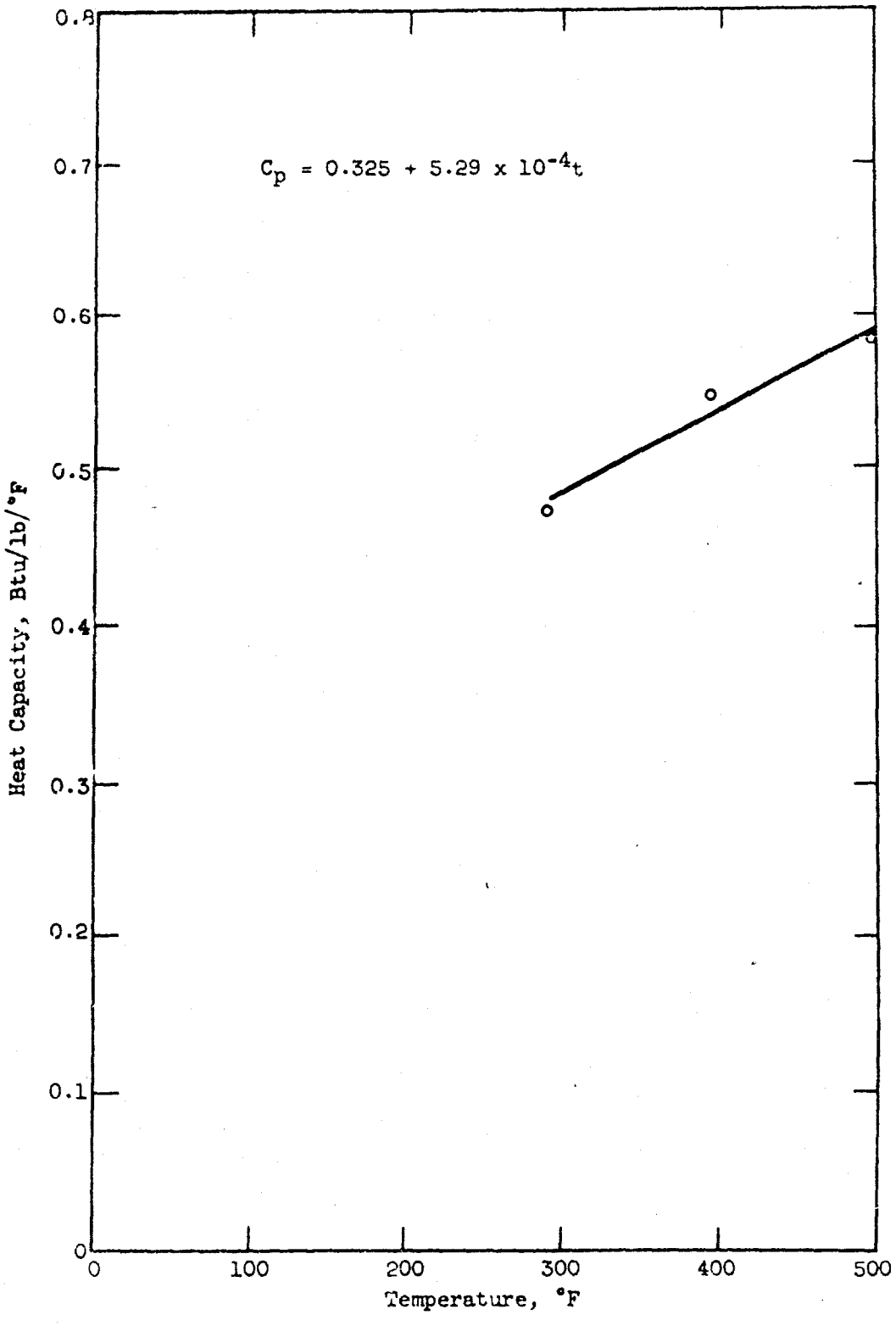

Fig. 24 - Heat Capacity of MLO-58-591

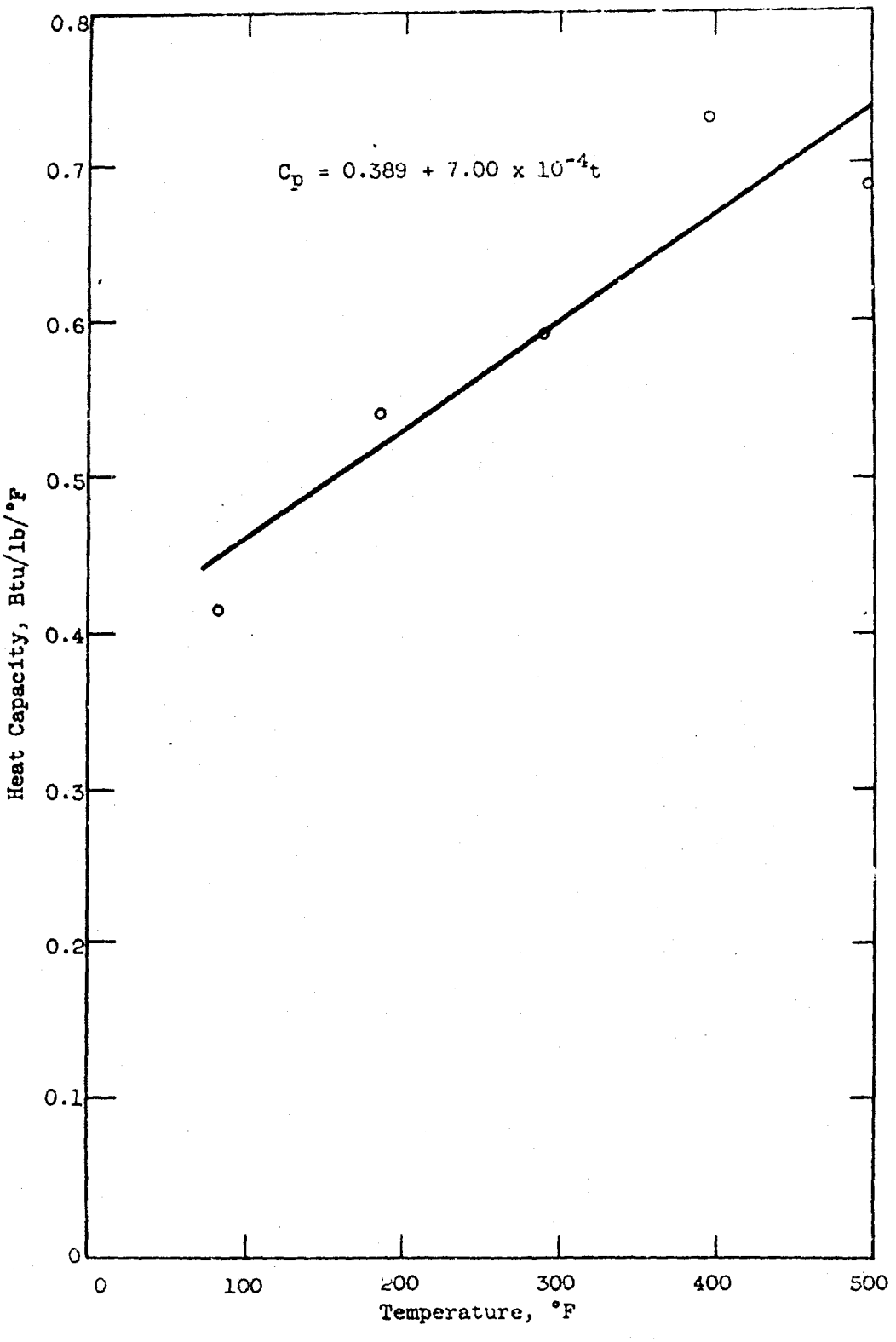

Fig. 25 - Heat Capacity of MLO-58-654

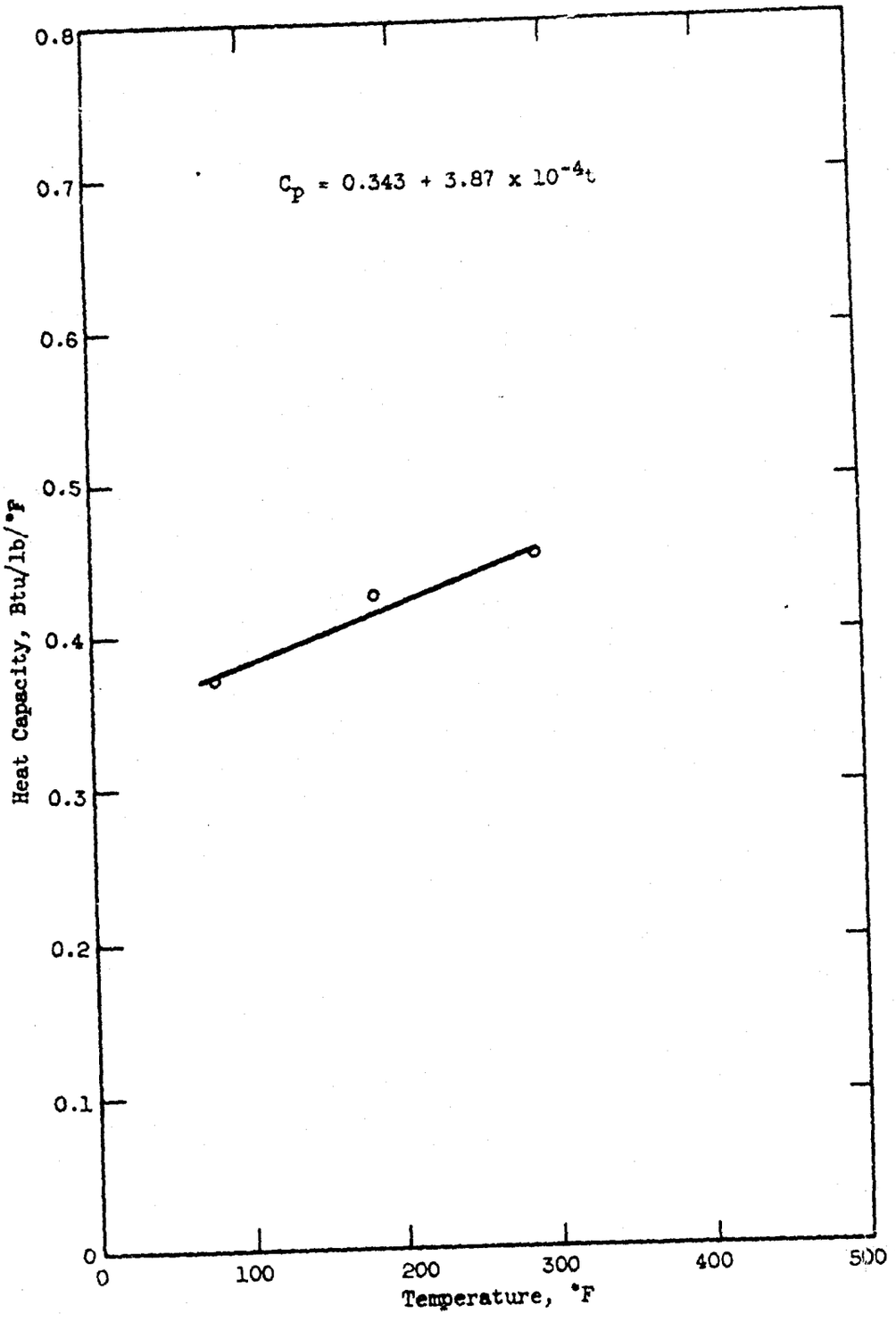

Fig. 26 - Heat Capacity of MLO-58-S58

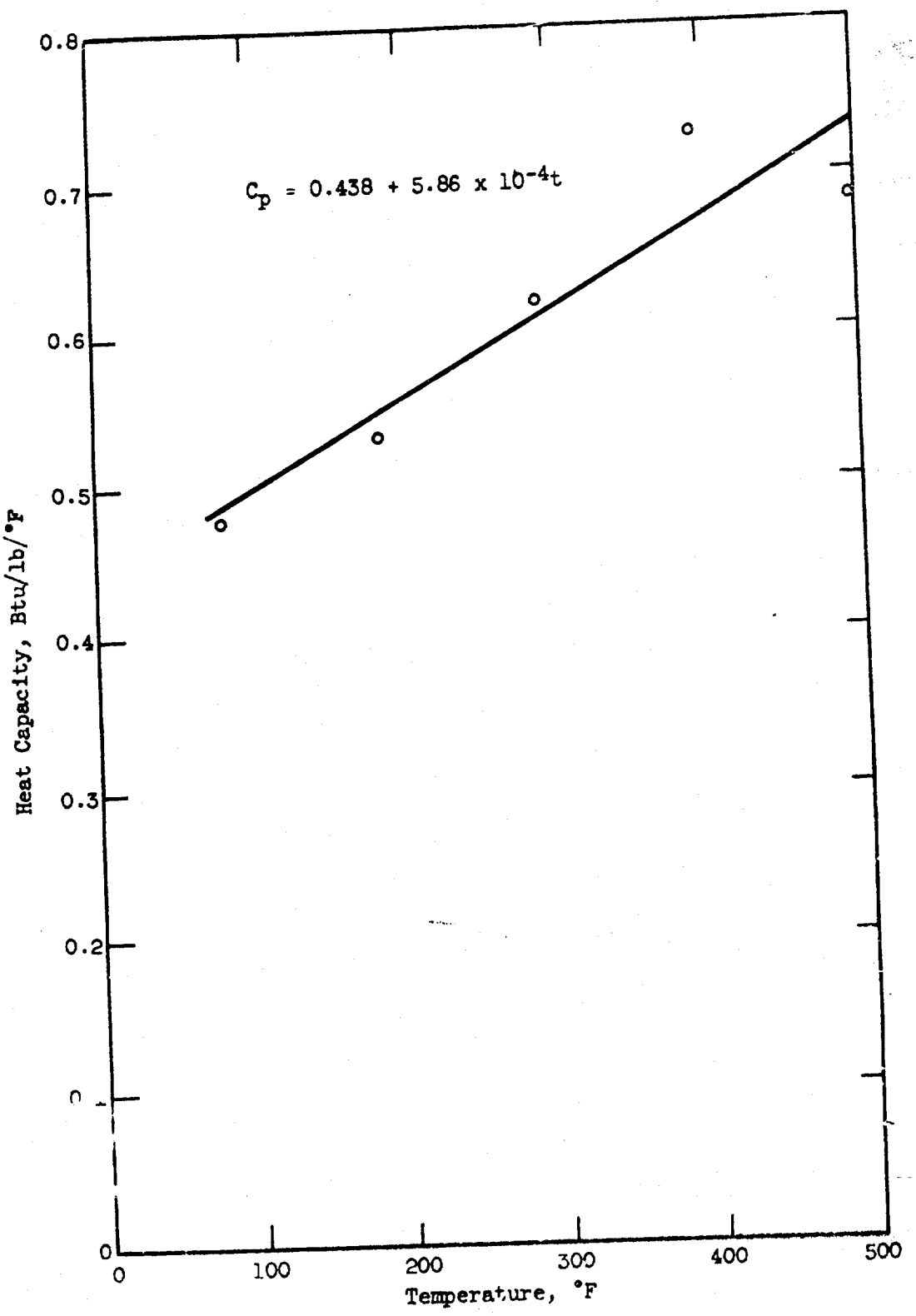

Fig. 27 - Heat Capacity of O-56-3N

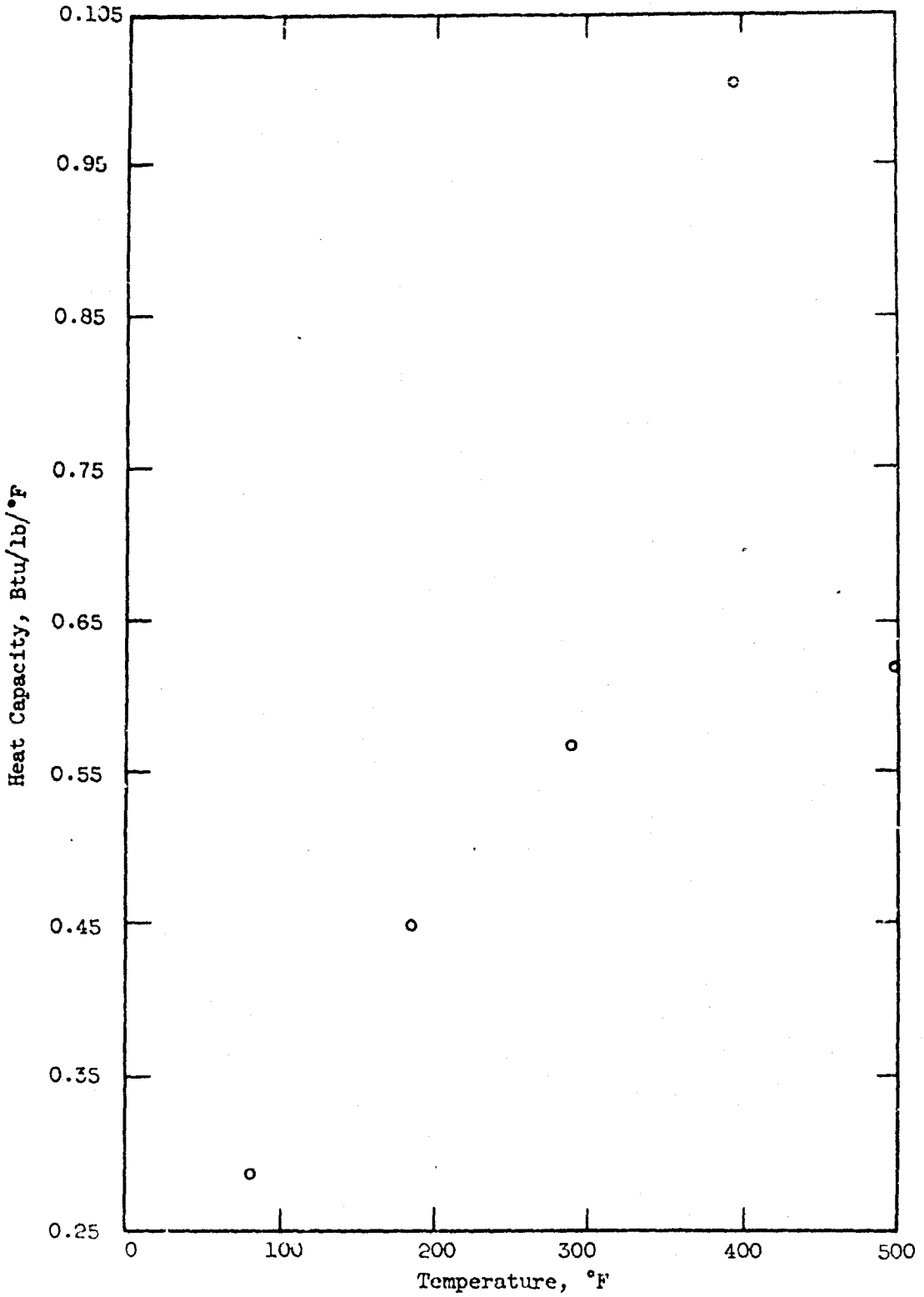

Fig. 28 - Heat Capacity of 0-57-3U

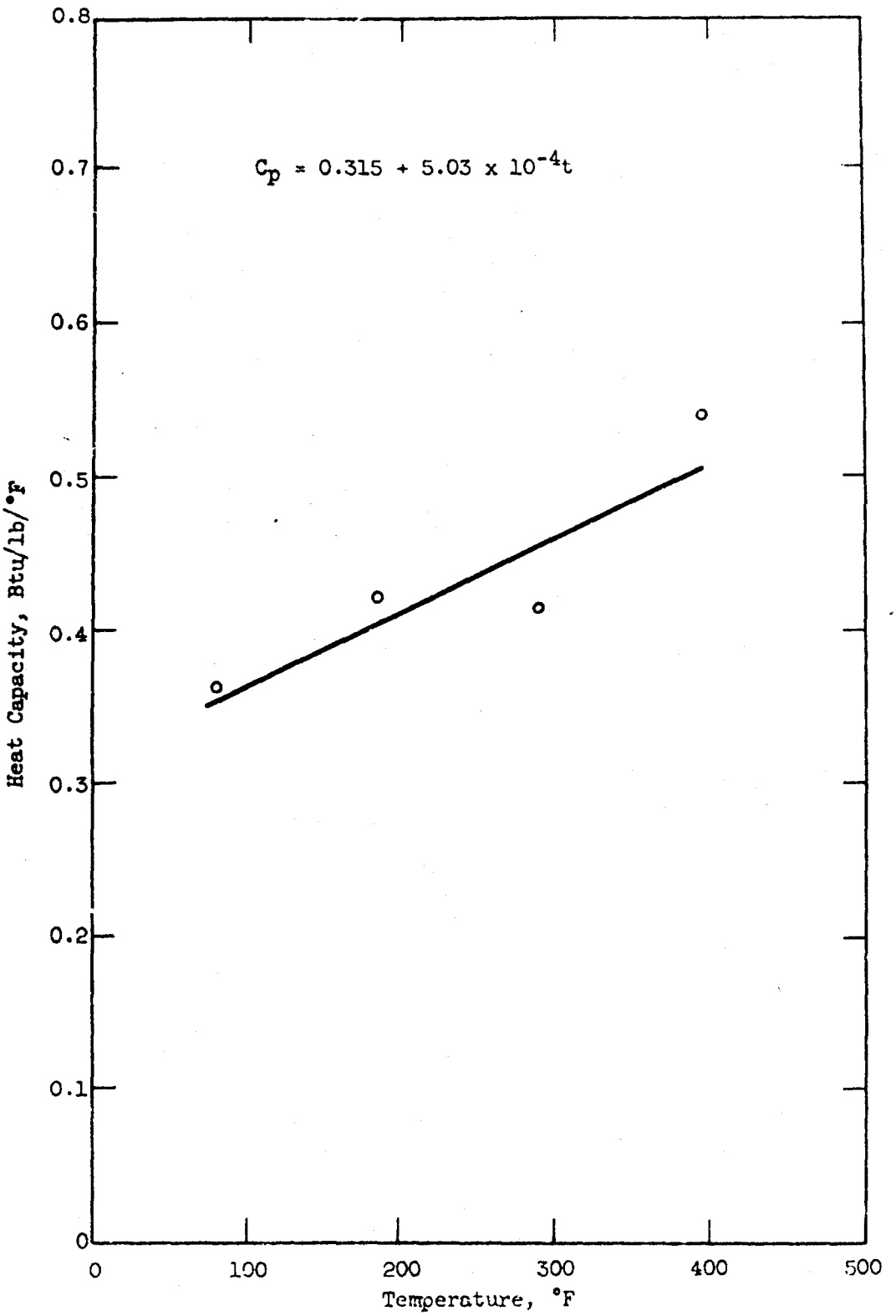

Fig. 29 - Heat Capacity of 0-57-19

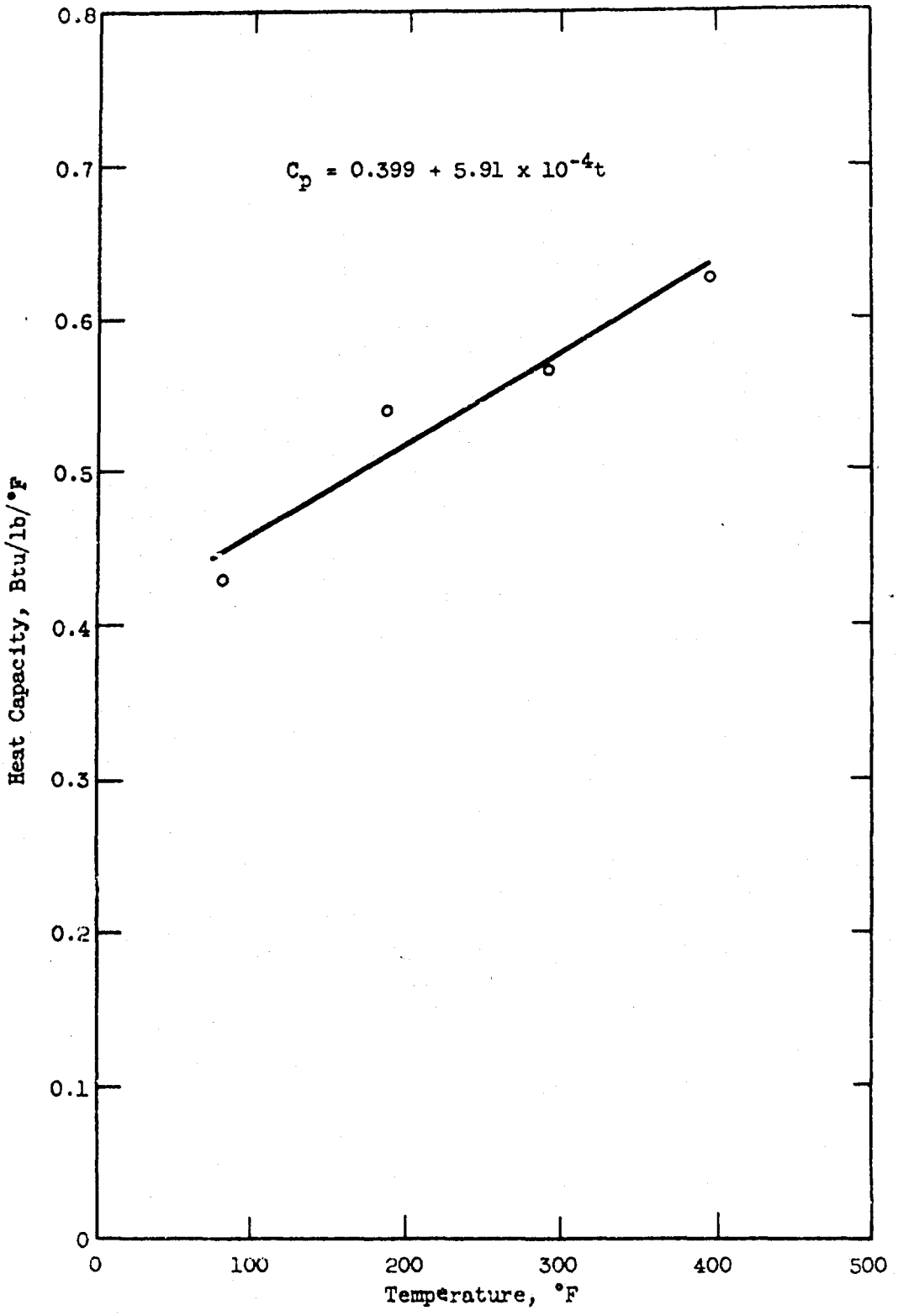

Fig. 30 - Heat Capacity of O-57-37

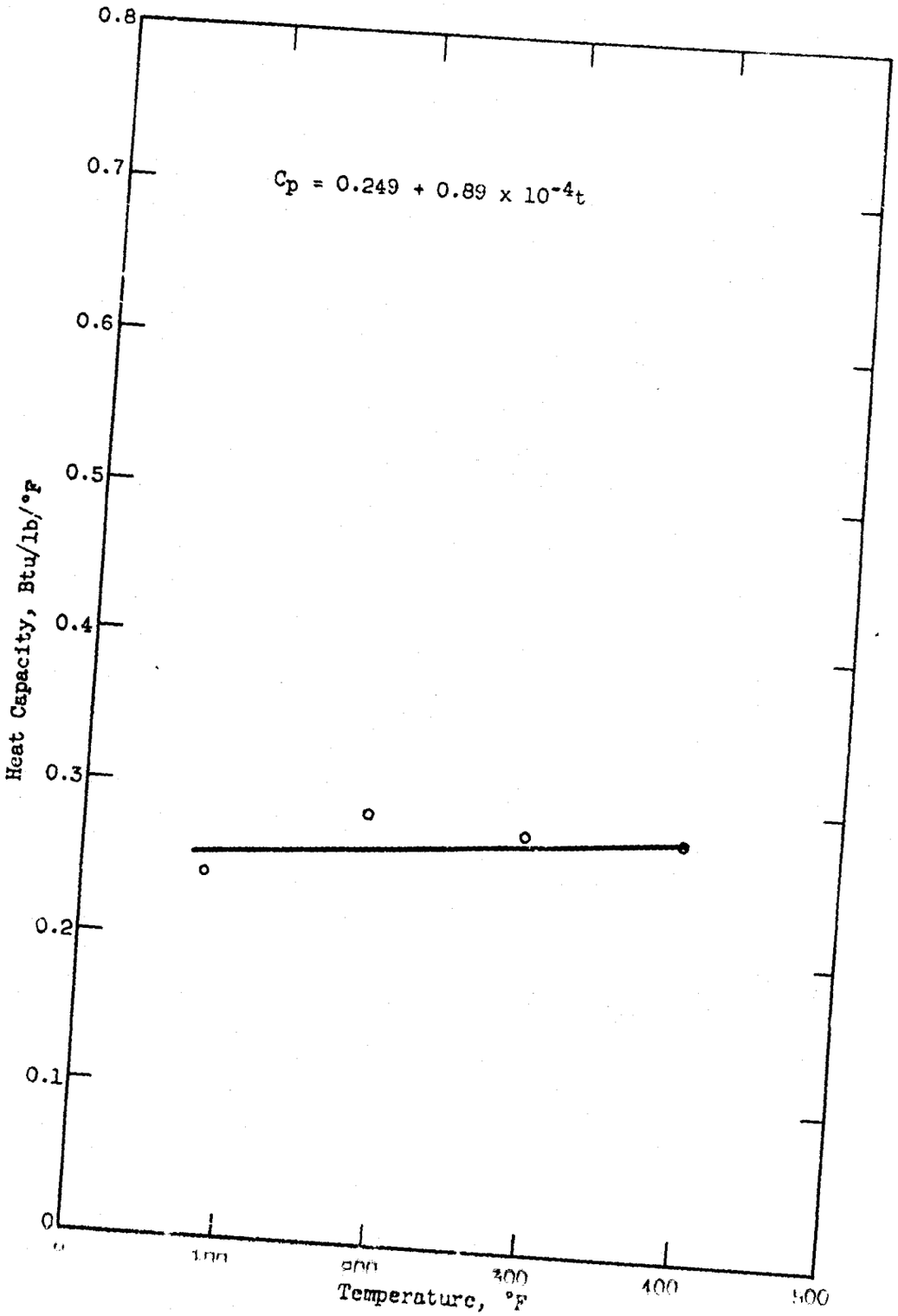

Fig. 31 - Heat Capacity of LRO-1

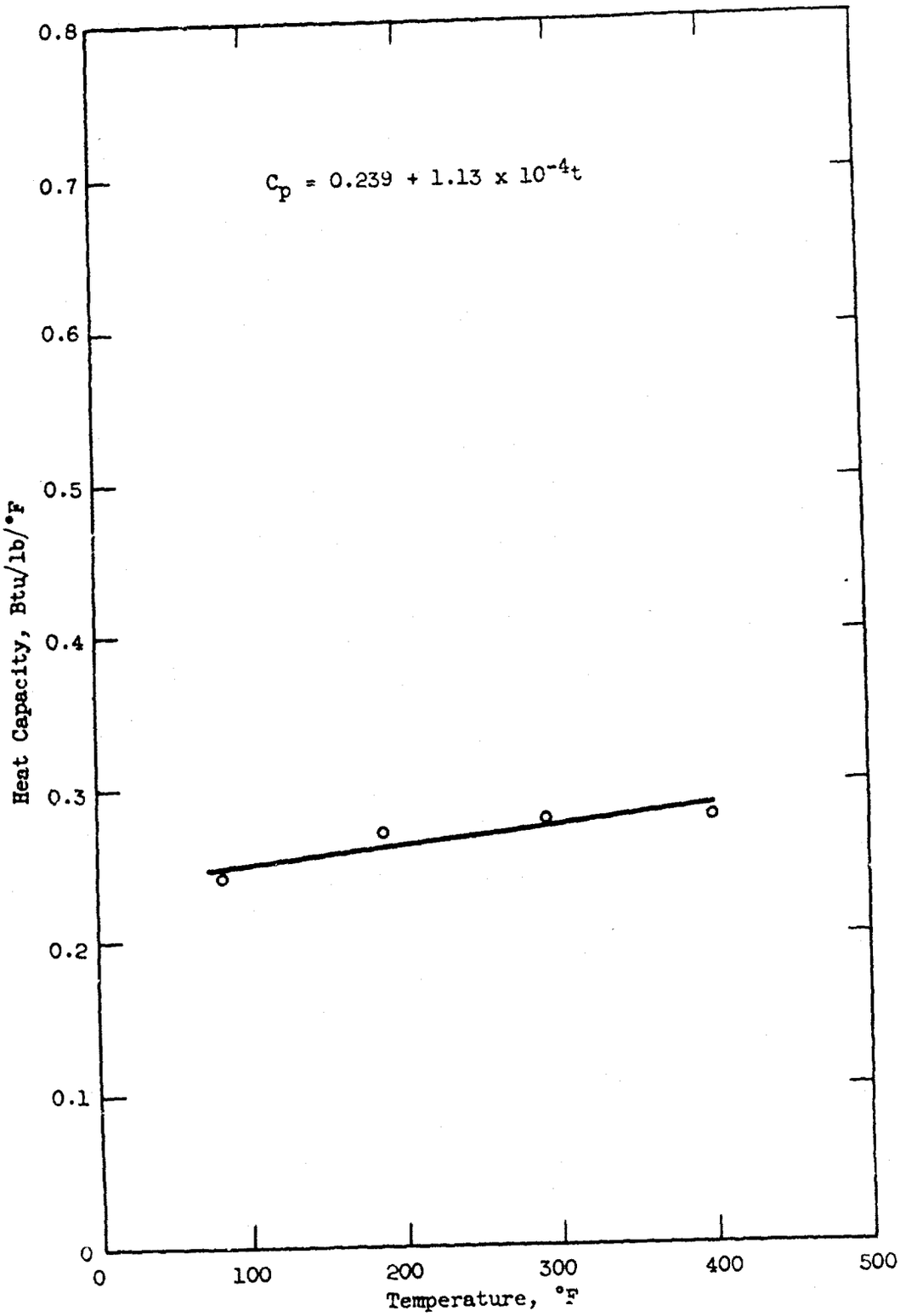

Fig. 32 - Heat Capacity of LRO-2

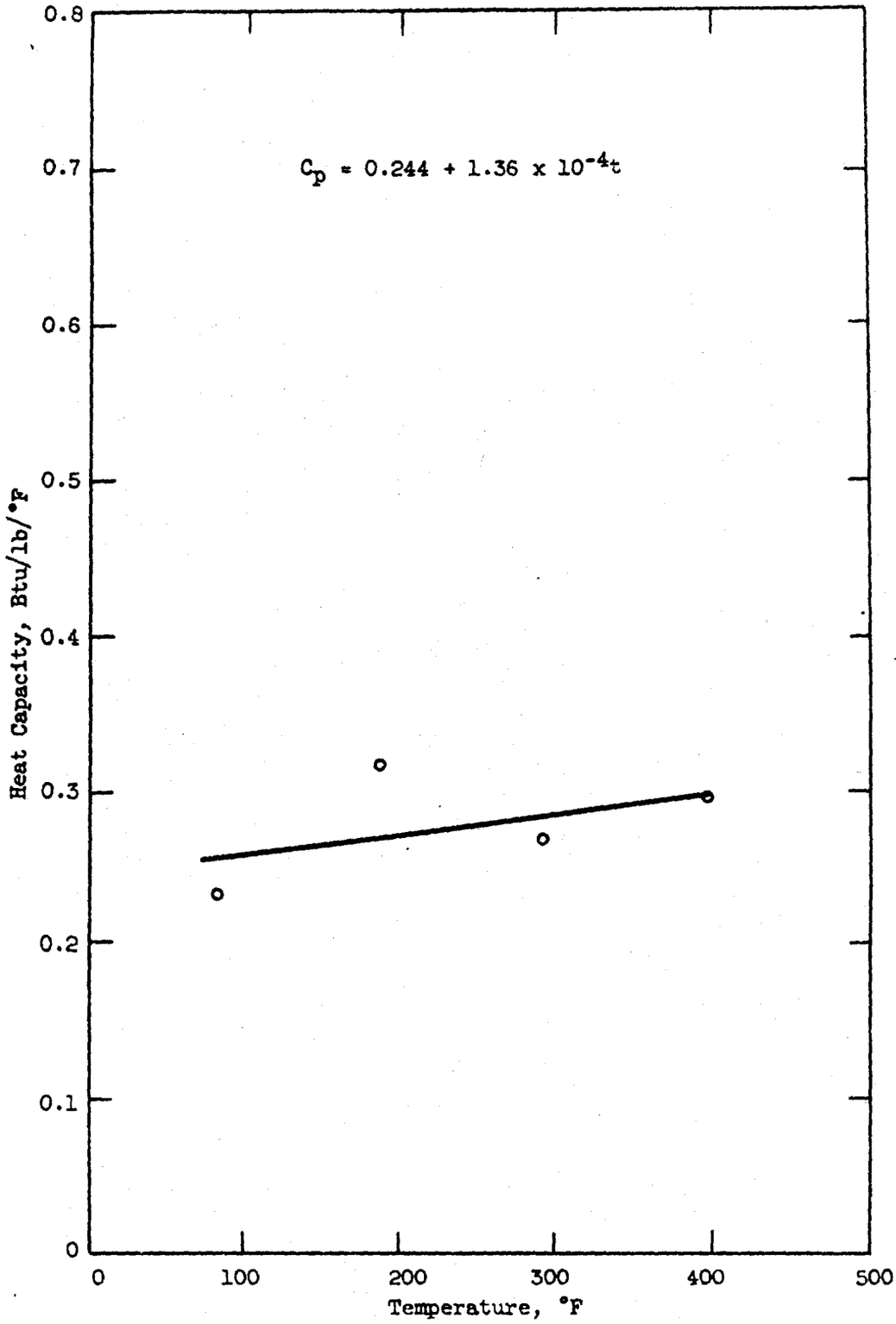

Fig. 33 - Heat Capacity of LRO-4

IV. EXPERIMENTAL

A. Equipment

The components of the calorimeter are illustrated in Fig. 34. The various parts as identified by number are: cold trap (1), Dewar (sample holder) (2), mercury reservoir (3), Dewar top and stirrer motor (4), sample heater (5), and stirrer (6). The individual calorimeters are constructed of Pyrex glass. Metal straps are used to attach and support the glassware.

The volume of the Dewar portion is about 250 ml., and the volume of the mercury reservoir is about 150 ml. The connection from the Dewar jacket to the reservoir consists of 2-mm. diameter tubing and a 2-mm. stopcock to provide complete transfer of the mercury from the Dewar jacket into the reservoir. The bore of the stopcocks on the cold trap and the mercury reservoir is not critical.

The Dewar top is constructed from pressed asbestos insulating board. It serves as a cover and as a support for the motor-stirrer and sample heater. The sample heater is approximately a 140-ohm element formed by winding No. 32 B & S gage Nichrome wire on a porcelain base. The heater element is connected to copper leads enclosed in glass tubes. After the electrical connection is made, the glass tubes and heating element base are sealed with Sauereisen compound. The stirrer is a flat half-circle piece of stainless steel, which is connected through a reduction gear to the 6 v. DC motor.

The heater energy is supplied by a constant voltage transformer. The potential (about 14 v.) and the electrical current (80 to 140 ma.) supplied to the heater are read to the nearest 0.01 v. and 0.001 amp. An electrical timer, reading to the nearest 0.1 sec., is used for determining the necessary time intervals. The temperature of the sample is measured with a Fiske differential thermometer (thermistor type). The sensitivity of this instrument depends upon the temperature range. The minimum detectable temperature changes are $\pm$ 0.002°F at low temperature and $\pm$ 0.006°F at high temperature. A mechanical vacuum pump is used to obtain a vacuum of about 10^{-3} mm. Hg on the Dewar jacket.

To shorten measurement time, four calorimeter units similar to the one illustrated in Fig. 34 were constructed. These units are mounted in a large thermostat, which is equipped for constant temperature control over the 70 to 500°F range.

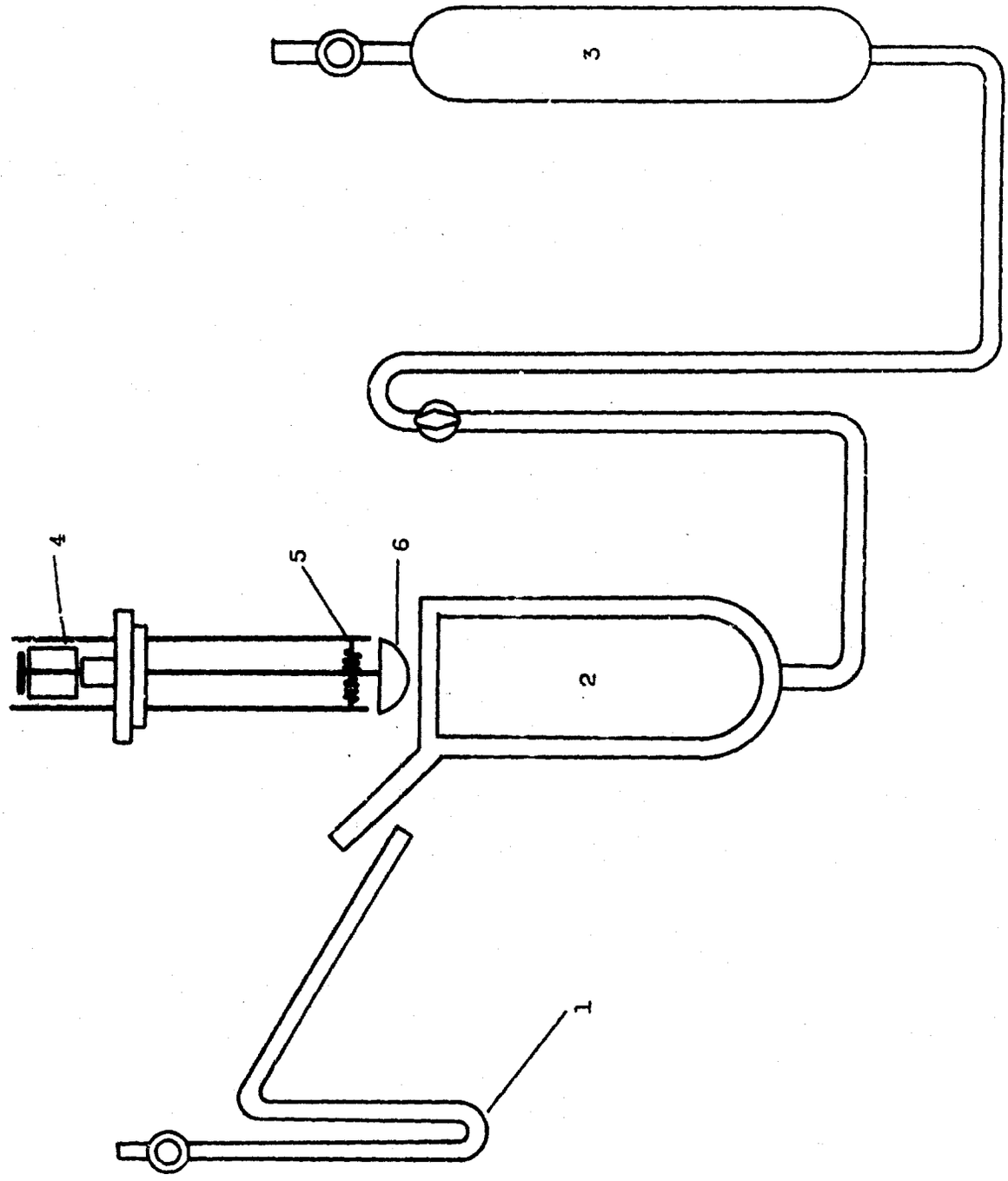

Fig. 34 - Calorimeter

B. Procedure

A sample (either 75 or 150 ml.) of the test liquid was accurately measured into the Dewar and the top-stirrer-heater unit set in place. When the large thermostat had reached the selected measurement temperature, the calorimeter unit was lowered into the thermostat. The stirrer was started and the temperature sensing probe was inserted. The mercury in the Dewar jacket rapidly equalized the sample temperature to that of the thermostat. At this point the mercury was pumped to the reservoir, the cold trap was attached to the Dewar and immersed in liquid nitrogen, and the Dewar jacket was evacuated. The expansion of the gases and evaportaion of residual mercury in the Dewar jacket always resulted in a fast sample temperature change of 1 to 2°F. To avoid errors from this initial heat transfer, measurements were started until 2 min. after applying vacuum. Experience showed that after this 2 min. equilibration period the heat transfer from the calorimeter was slow and uniform.

Starting with zero time (2 min. after applying vacuum) the following operations were performed and the data recorded. Thirty seconds - sample temperature recorded; 110 sec. - sample temperature recorded and heater turned on; 140 sec. - sample temperature recorded; 150 sec. - voltage and current recorded; 210 sec. - same as 150 sec.; 220 sec. - sample temperature recorded and heater turned off; 250 sec. - sample temperature recorded; and 330 sec. - sample temperature recorded.

There were four reasons for strictly adhering to this order of measurement. First, the calorimeters were not absolutely adiabatic but exhibited a slow linear heat loss. This rate of heat loss as measured by temperature decrease was 2 to 4°F per hour for low temperatures and 16 to 18°F per hour at high temperatures. Secondly, there was a small lag time in the temperature measuring equipment. Thirdly, the rate of temperature change was used to calculate the heat capacity. Fourth, equal time intervals on heating and cooling facilitated calculations.

A statistical design was chosen for these measurements and sample numbers in the design were assigned at random to the oils.

Volumes of 75 ml. and 150 ml. were assigned so that for the same oil the different volumes fell in different calorimeters.

C Calculations

As stated in the previous section, the preliminary runs with diphenyl ether showed that there was a definite but small heat loss from the calorimeters. The rate of heat loss varied from 2 to 4°F per hour at low temperatures to 16 to 18°F per hour at high temperatures. Experimental work further showed that these losses were uniform (constant rate). Therefore, the following method of calculation was devised to correct for these losses.

Assuming that temperature equilibrium is achieved rapidly and that the heat loss rate $\left(\frac{dH}{dt}\right)$ is constant for a given system at a given temperature, the following equation holds over a limited range:

$$\text{Net heat loss} = \int_0^t \left(\frac{dH}{dt}\right) dt = b_c \, \Delta t(w_s s_s + w_c s_c) \qquad (1)$$

where b_c is the temperature loss per second, w_s and w_c are the weight of the sample and calorimeter components, respectively, s_s and s_c are their respective heat capacities and Δt is time in seconds.

Likewise, the net heat gain can be expressed as:

$$\text{Net heat gain} = b_H \, \Delta t(w_s s_s + w_c s_c) \qquad (2)$$

where b_H is the temperature rise per second.

The total heat put into the system should equal the sum of the observed gain and loss, thus:

$$EI \, \Delta t = b_H \, \Delta t(w_s s_s + w_c s_c) + b_c \, \Delta t(w_s s_s + w_c s_c) \qquad (3)$$

or

$$EI \, \Delta t = (b_H + b_c)(w_s s_s + w_c s_c) \, \Delta t \qquad (4)$$

where E is the potential applied to the heater and I is the current in the heater.

Solving Eq. (4) for the heat capacity of the sample yields:

$$s_s = \frac{1}{w_s}\left[\frac{EI}{b_H - b_c} - w_c s_c\right] \tag{5}$$

The weight of the samples, w_s, and the energy input, EI, are measured directly. The values for the rates of temperature rise, b_H, and loss, b_c, are determined from the readings indicated in the experimental procedure.

Calculations of calorimeter constants and specific heat equations: An assumption is made that the calorimeter constants are functions of test temperature and are relatively independent of sample size. This assumption seems reasonable when one realizes that although surface area increases with volume, the rate of heat loss per unit area will decrease. The latter is of course due to the fact that with a constant power input, the increase in sample temperature varies inversely with sample weight.

With the above assumption, we can express the results of a single determination (say for oil, i, in calorimeter, j, at temperature, T) as

$$\text{Observed}\left(\frac{\text{Btu}}{^\circ\text{F}}\right)_{ijT} = W_{ij}(C_p)_{iT} \cdot K_{jT} \cdot E_{ijT} \tag{6}$$

where i, j, T denote oil, calorimeter and temperature

W = weight of oil

C_p specific heat

K = calorimeter constant

and E = a random error

Both C_p and K are functions of temperature and can be approximated by polynomials in T. Hence Eq. (6) can be rewritten as

$$E_{ijT} = Z_{ijT} - \left\{ W_{ij}a_i + m_j \right\} - \left\{ W_{ij}b_i + n_j \right\} T - \left\{ W_{ij}c_i + o_j \right\} T^2 - \ldots \quad (7)$$

where Z_{ijT} is the observed reading in Btu per degree Fahrenheit.

Because only five temperatures were used in the evaluation, a maximum of five coefficients can be estimated in each polynomial. As C_p and K are usually adequately represented by quadratic equations, the analysis has been limited to computing and evaluating second degree equations.

The best estimates of these constants are those values which minimize the sum of the squares of the E_{ijT}. These estimates are obtained by squaring Eq. (7); summing over all i, j, and T; taking the partial derivatives with respect to each coefficient; equating each equation to zero; and solving the resultant simultaneous equations. The number of equations will be equal to three times the number of oils plus three times the number of calorimeters. In this series this would be a set of 105 equations.

As the temperatures were at equal intervals the method of orthogonal polynomials' values can be used. This gives three sets of simultaneous equations in unknowns equal to the sum of number of oils and calorimeters. The solution of these equations ordinarily would be onerous and time consuming. However, the use of two volumes (75 and 150 ml.) for each oil enables one to immediately reduce each set of equations to four equations containing only calorimeter constants. These four equations can be easily solved and the substitution of the solution in the original set yields the oil constants for Eq. (7). The appropriate combination of the a_i and b_i yields the linear specific heat lines as given in Figs. 1 through 33.

PART TWO - LATENT HEAT OF VAPORIZATION

I. INTRODUCTION

The latent heat of vaporization of a pure compound is one of the more difficult physical properties to determine accurately. For many pure compounds, the latent heat values found in the literature show considerable variation and often are accompanied by the notation "approximate" or "calculated".

No real claim to accuracy is made unless the experiments have used the direct vaporization method in an adiabatic calorimeter where the measurement of heat input is electrical.

Where the problem involves the determination of latent heat for mixtures, the difficulties are doubly compounded. There are now three latent heats to consider: (1) integral isobaric, (2) integral isothermal, and (3) differential. Composition remains constant in the integral (total vaporization) process, while changing composition is experienced in a differential process. Integral latent heats can be determined experimentally in an adiabatic flow calorimeter, while the differential latent heat is usually calculated.

The materials under study in this report are all mixtures, to some degree. The integral isobaric heat of vaporization is therefore the desired latent heat property, and the true value of this property can only be determined in a flow calorimeter.

In general, adiabatic flow calorimeters require a substantial quantity of test material, say 0.5 to 1.0 gallon per experimental test. At the time, such quantities of these test materials were not available. As a compromise, the static apparatus used here was designed to require only 100-120 cc. of test material per experiment. The results obtained are therefore only rough indicators of differences in latent heats of the various test materials, and cannot be assumed to represent the true integral isobaric heat of vaporization.

II. SUMMARY AND CONCLUSIONS

Since the latent heat of vaporization measurements were made on impure compounds (mixtures) only relative values of the heat of vaporization of the phenyl ethers are given.

III. DISCUSSION AND RESULTS

The experimental equipment and technique proved to be reliable with respect to reproducibility of experimental data on pure compounds. An example of this reproducibility is shown in Table IV for pure phenyl ether. The latent heat of vaporization of this compound has been calculated as 66.16 cal/gm at the normal boiling point of 259°C.

Table V presents our experimental data for the test materials. An experimental molecular weight is given for each material. These data were obtained for the "as received" samples by the boiling point elevation method using benzene. There is an increase in average molecular weight for each of the three irradiated samples, compared to its nonirradiated counterpart.

The data indicate a very significant change in apparent latent heat between the irradiated and nonirradiated samples. Note, particularly, that the order of magnitude of this change is a factor of 14 to 16 times the latent heat of the nonirradiated sample for the two higher boiling mixtures. The boiling point range of MLO-58-589 and 591 was approximately the same, although MLO-58-588 and -590 had boiling points comparable to the pure phenyl ethers, as shown in Table VI.

It is believed that a combination of all possible heat losses from the apparatus, as outlined in other parts of this report, could not account for the change in apparent latent heat cited above. The conclusion follows that there is a significant change in the true isobaric latent heat of vaporization of these samples following irradiation.

To clarify the statement that heat losses from the apparatus could not account for the large difference in apparent latent heat between irradiated and nonirradiated samples, the following approximation is made.

TABLE IV

HEAT OF VAPORIZATION OF PURE PHENYL ETHER

Run No.	Uncorrected ΔH_T/g, cal/gm	B.P., °C	Barometer mm. Hg	Room Temp., °C
1	73.8	256.2	742.7	25.5
2	73.9	256.6	754.9	25.7
3	73.7	256.3	756.2	26.6

TABLE V

LATENT HEAT OF VAPORIZATION AND MOLECULAR WEIGHT OF TEST SAMPLES

Number MLO-58-	Mole Wt. Theor.	Mole Wt. Exp.	Pre Evap. w/o	Uncorrected ΔH_T/g, cal/gm	B.P., °C	Bar. mm. Hg	Room Temp., °C
586	170	169	Trace	71.8	254.5	741.4	27.1
"	"	"	"	74.8	255.0	748.2	27.3
587(R)	"	184	19.1	136.6	249.6	740.4	28.0
588	262	281	7.1	73.8	376.8	744.3	26.2
589(R)	"	292	4.0	1,024.3	352-368	744.1	28.2
590	354	328	?	98.9	457	753.0	26.7
591(R)	"	345	1.8	1,632.7	359-362	747.3	25.6

TABLE VI

BOILING POINTS OF PURE PHENYL ETHERS

	B.P., °C
Phenyl Ether	259
1,4-Diphenoxy benzene	384
Bis(p-phenoxy phenyl) Ether	462

Let us assume that (1) the true latent heat of the fraction evaporated is the same with or without irradiation, (2) the heat capacity of the sample remaining is approximately 0.5 cal/gm-°C, and (3) radiation losses due to the temperature rise during the test are negligible compared to sensible heat losses to the vapor jacket. On this basis, we can calculate the over-all heat transfer coefficient for sensible heat transfer between the test cell and the cooler vapor jacket surrounding it.

The test on Bis(p-phenoxy phenyl) ether will be used for illustration. The following data are taken from the data sheet for ML0-58-591.

$$\Delta H_T = \frac{(6.58 \text{ v.})(0.84 \text{ a.})(330.4 \text{ sec.})}{4.186} = 436.3 \text{ calories}$$

Initial sample weight	11.466 gm.
Less pre-evaporation	0.202
	11.264
Less grams evaporated	0.267
Not evaporated	10.997 gm.

Assume the temperature rise of 3°C was present throughout the test, and that the heat of vaporization of the fraction vaporized is about 100 calories per gram.

1. Heat for vaporization = $\Delta H_V = (100)(0.27) = 27$ calories

2. Sensible heat of remainder = $\Delta H_S = (11)(0.5)(3) = 16.5$ calories of sample

3. Sensible heat transferred = $Q = 436.3 - 27 - 16.5 = \underline{392.8}$ calories

4. $\frac{Q}{t} = q = UA\Delta t$

The area, A, for heat transfer from the test cell of 7/8 inch diameter and 2-3/4 inch length is

5. $A \cong \pi DL + \frac{2\pi D^2}{4} = \pi D \left[L + D/2\right] = 0.06085 \text{ ft}^2$

The heat transfer coefficient is then

$$6.\quad U = \frac{q}{A\Delta t} = \frac{(392.8)(3600)}{(252)(330.4)(0.06085)(3)(1.8)}$$

$$= \underline{\underline{516.8}}\ \frac{\text{Btu}}{\text{hr -ft}^2\text{-°F}}$$

A normal to high heat transfer coefficient for the configuration of the test cell and surrounding vapor jacket would be of the order of 100-150, rather than 517. The conclusion follows that the heat of vaporization for the irradiated sample is significantly higher than 100 cal/gm.

Working backward from an assumed U of 150, the order of magnitude of the latent heat may be calculated.

$$7.\quad \Delta H_V = \Delta H_T - \Delta H_S - Q$$

$$= 436.3 - 16.5 - \frac{(150)(0.06085)(3)(1.8)(252)(330.4)}{3600}$$

$$= 305.8 \text{ calories}$$

$$8.\quad \frac{\Delta H_V}{g} = \frac{305.8}{0.267} = \underline{\underline{1145.3}} \text{ cal/gm for MLO-58-591}$$

The increase in molecular weight suggests that some polymerization of the test materials has occurred during irradiation. Certain observations made in these tests indicate that a further change occurred on heating these materials to their boiling point, although the changes were not investigated and may be due in part to oxidation in the air.

IV. EXPERIMENTAL

A. Equipment

The latent heat of vaporization apparatus used in these experiments is shown schematically in Fig. 35. The numbered parts are:

(1) Receiver tube
(2) Vapor jacket
(3) Condenser arm
(4) Heater leads, B & S No. 14 copper wire
(5) Annular reboiler
(6) Receiver baffle
(7) Adiabatic test cell
(8) Test cell resistance heater
(9) Annular heater
(10) Base reboiler
(11) Glass insulating and support ring
(12) Base heater

Power input to the test cell resistance heater was controlled and measured by the circuit shown schematically in Fig. 36. This circuit afforded positive coordination of the timer, since both timer and power circuits closed and opened simultaneously through one double pole knife switch. The power circuit gave excellent control of input heat over a substantial watt-second range.

B. Procedure

Liquid samples required no special treatment prior to loading the cell and reboilers. Solid samples were ground in a mortar, melted, and loaded as a liquid.

The test cell was tare weighed, loaded and reweighed, and assembled on the receiver tube. The annular reboiler was filled to the top by tilting the apparatus and allowing the liquid sample to run down the wall of the calorimeter. When the annular reboiler was filled, additional sample fluid ran down into the base reboiler.

The calorimeter was placed upright on the glass insulating and support ring and the base heater. A water condenser was attached to the condenser arm. The calorimeter and condenser were flushed out with nitrogen to displace all air. The test cell and receiver tube assembly was then

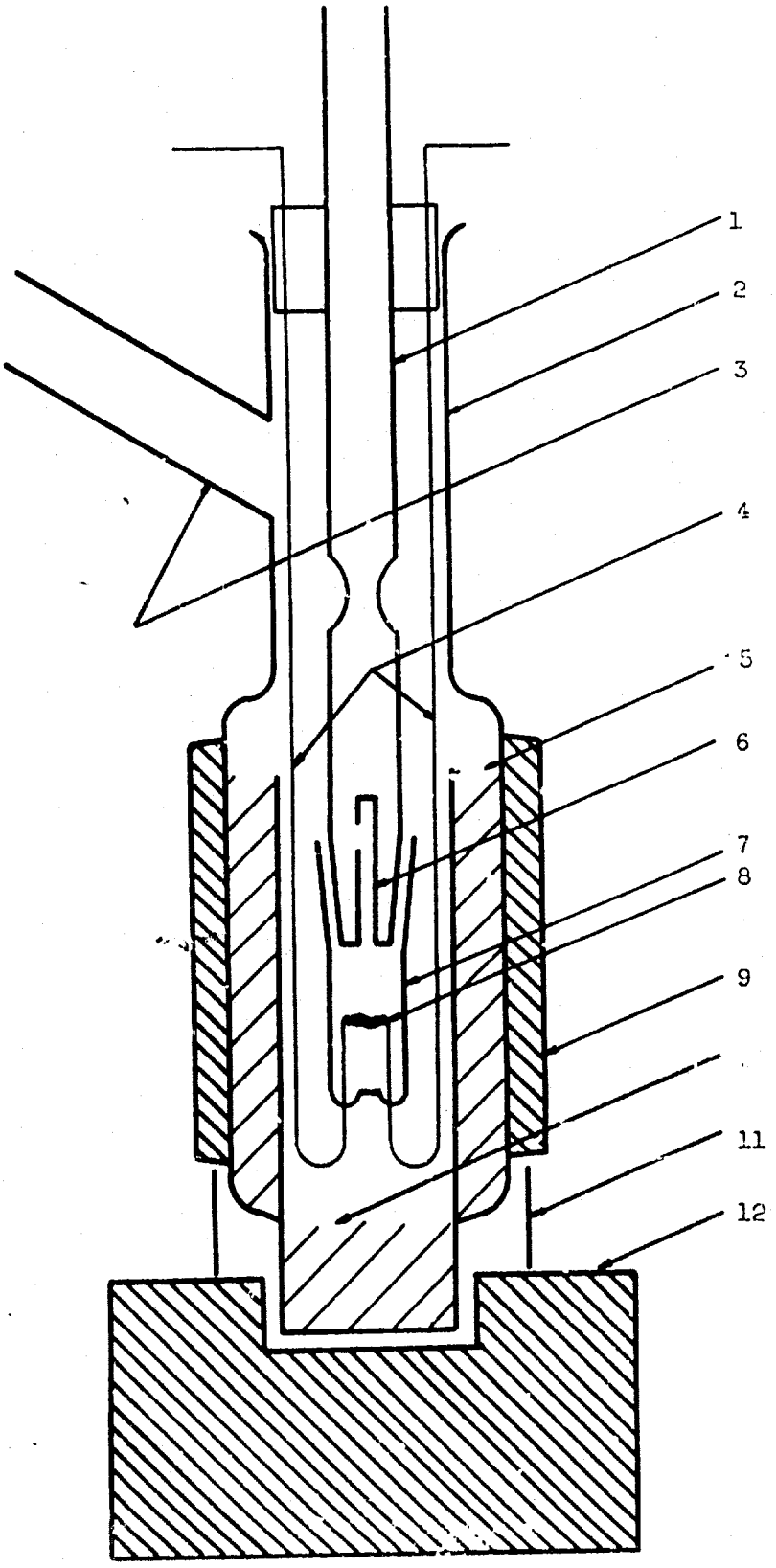

Fig. 38 - Latent Heat of Vaporization Calorimeter

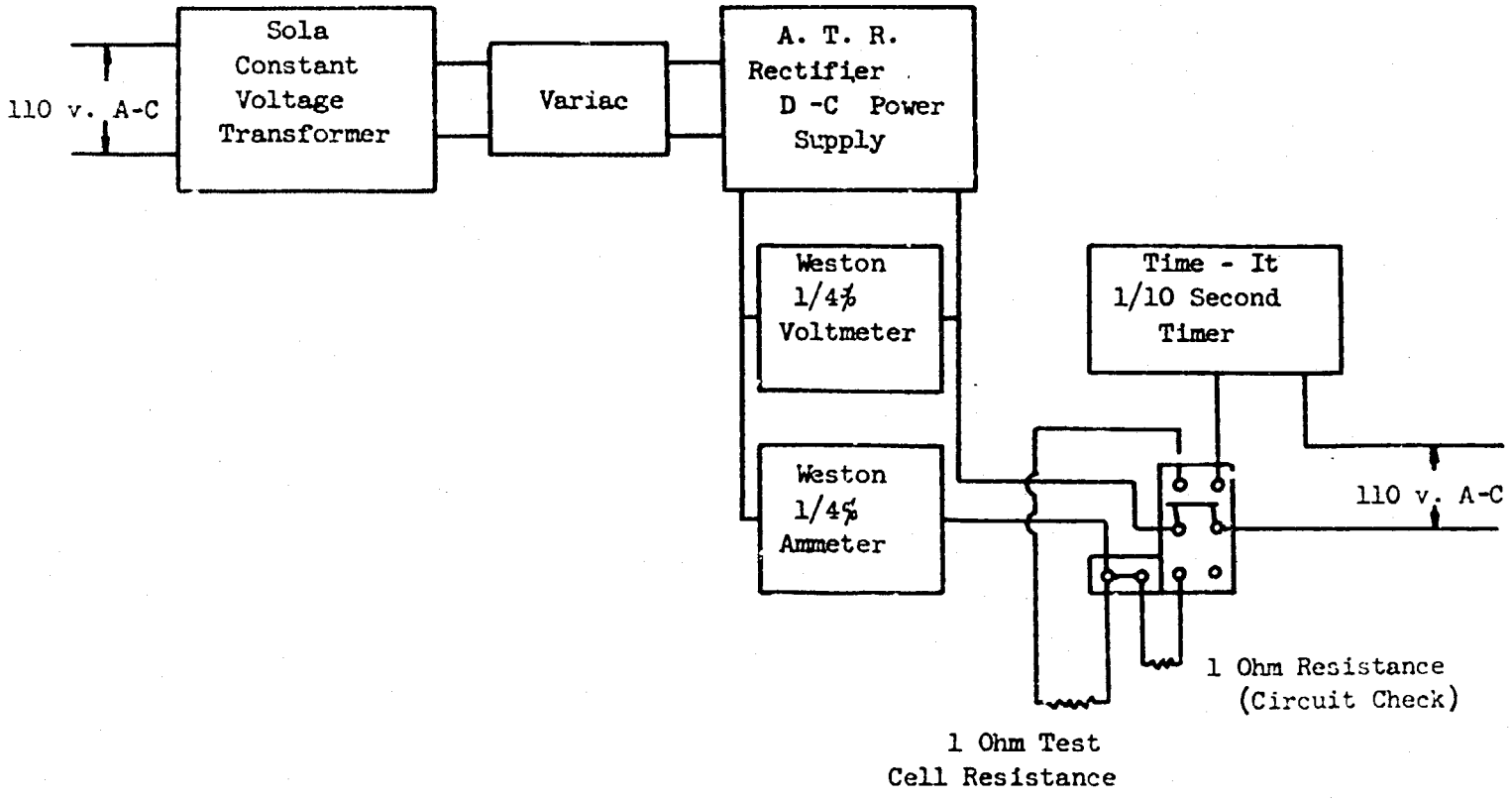

Fig. 36 - Power Measuring and Control Circuit

lowered into the calorimeter. Electrical connections were made to the three heaters and the annular wall thermocouple. An iron-constantan thermocouple was placed in the receiver tube, touching the base of the tube.

The assembled calorimeter was heated gradually to bring it up to the boiling temperature without superheating. Boiling was continued until a constant temperature was indicated by the receiver thermocouple. Constant temperature boiling was continued for an additional 15-minute period to make certain equilibrium was obtained. The calorimeter test cell was then cooled down and reweighed to indicate the weight of the test sample that had fractionated into the receiver tube.

After reassembly of the entire apparatus, the calorimeter was slowly heated until the equilibrium boiling point was reached and a steady-state boil-up attained in the vapor jacket.

The power measuring circuit was turned on, warmed up and adjusted by using the auxiliary resistance, which approximated the resistance of the test cell heater. The double throw knife switch was then closed to the opposite side, simultaneously starting the timer and the power input to the test cell.

During the test period, time, temperature, potential and current were read and recorded at frequent intervals. The test period usually lasted five or more minutes.

At the end of the test period, all power circuits were opened. The receiver tube and test cell were removed from the vapor jacket and cooled down to room temperature. The test cell was weighed to determine the amount of material vaporized during the test.

C. Calculations

The total heat input is calculated as follows:

$$\frac{\Delta H_T}{g} = \frac{EIt}{g(4.186)} \text{ , in gram-calories, 15° per gram} \qquad (8)$$

where

E = volts = joules/second
I = amperes
t = seconds
4.186 = conversion factor, Joules/gm-cal, 15°
g = grams evaporated

The total heat input accounts for latent heat of vaporization, plus all heat losses, or

$$\frac{\Delta H_T}{t} = \frac{g(\Delta Hv)}{t} + \frac{\Delta H_L}{t} = \frac{EI}{4.186} \text{ , in gm-cal , 15° per second} \qquad (9)$$

For pure compounds, the only possible heat loss from this apparatus is radiation loss in an upward direction, since the test cell is surrounded by vapors at the boiling point in all other directions. This loss would be a function of the difference of the fourth powers of the boiling point temperature and the room temperature in °K, or

$$\frac{\Delta H_L}{t} = C(T_B^4 - T_R^4) \qquad (10)$$

The calorimeter constant, C , could be determined by experiment. A number of pure compounds having accurately known latent heats could be tested to determine the heat loss at various temperatures within the range of interest. $\frac{\Delta H_L}{t}$ is then plotted against $(T_B^4 - T_R^4)$ on rectangular coordinates as a straight line. The slope of the line is the calorimetric constant, C .

In attempting to determine latent heats of mixtures in this apparatus, other heat losses are encountered for which we cannot hope to account. With batch fractionation occurring in the test cell, a temperature rise is experienced during the test period. This causes sensible heat losses to (1) the jacketing vapors, (2) that part of the sample not vaporized, and (3) the re-boiling of the vaporized part of the sample. There are also additional radiation losses in all directions.

It is conceivable that these additional losses could be several orders of magnitude larger than the single radiation loss encountered when testing pure compounds. Calibration of the calorimeter therefore serves no useful purpose where mixtures are concerned.

BIBLIOGRAPHY

1. Barger, J. W., Medved, T. M , Bolze, C. C., "Heat Capacity Determination of Mineral and Synthetic Engine Oils, Lubricants, Fuels, and Hydraulic Fluids in the Temperature Range 70°-500°F", WADC Technical Report 58-70, ASTIA Document No. 155630, June 1958.

APPENDIX I

IDENTIFICATION OF HEAT CAPACITY SAMPLES*

Sample No.	Identification	Source
1. MLO 56-200	Petroleum base hydraulic fluid	Pennsylvania State University
2. MLO 57-628	Octyl decyl tridecyl silane	Materials Laboratory, WADC
3. MLO 58-342	- -	- -
4. O-56-36 N**	Conoco 9372	Continental Oil Co.
5. O-56-36 U***	Conoco 9372	Continental Oil Co.
6. O-56-57 N**	RPM Aviation Turbine Oil-15	California Research Corp.
7. O-56-57 U***	RPM Aviation Turbine Oil-15	California Research Corp.
8. O-57-13	WS-2812	Esso Standard Oil Co.
9. O-57-36	A-2427	Monsanto Chemical Co.
10. O-58-6	[illegible]-258	Dow-Corning Corp.
11. O-58-8	DV-5248	E.I. duPont deNemours & Co.
12. O-58-12	L-825	Lehigh Chemical Co.
13. O-58-13	72449 C	R. M. Hollingshead Corp.
14. LRO-3	10-25	Halocarbon Products Corp.
15. Richfield L8-32	Richfield L8-32	Richfield Oil Corp.
16. Cal.Res.Fluid#341	- -	- -
17. MLO 58-418	Bis(p-phenoxy) benzene	Shell Development Co.
18. MLO 58-432	Bis(p-phenoxyphenyl) ether	Shell Development Co.
19. MLO 58-586	Phenyl ether	Shell Development Co.
20. MLO 58-587	Phenyl ether (irradiated)	Shell Development Co.
21. MLO 58-588	1,4 Diphenoxybenzene	Shell Development Co.
22. MLO 58-589	1,4 Diphenoxybenzene (irradiated)	Shell Development Co.
23. MLO 58-590	Bis(p-phenoxyphenyl) ether	Shell Development Co.
24. MLO 58-591	Bis(p-phenoxyphenyl) ether (irradiated)	Shell Development Co.
25. MLO 58-654	Mineral Oil, Hydrogenated Paraffinic	Pennsylvania State University
26. MLO 58-658	- -	- -
27. O-56-3 N**	WS-3085	Esso Standard Oil Co.
28. O-57-3 U***	"UCON" Lubricant LB-300-X	Union Carbide Chemicals Co.
29. O-57-19	Versilube F-50	General Electric Co.

IDENTIFICATION OF HEAT CAPACITY SAMPLES*(Concluded)

Sample No.	Identification	Source
30. O-57-37	CALRESEARCH 230	California Research Corp.
31. LRO-1	4-11 V	Halocarbon Products Corp.
32. LRO-2	11-14	Halocarbon Products Corp.
33. LRO-4	AO-213	Fluro-Chem Corp.

* Samples supplied to Midwest Research Institute under Contract No. AF 33(616)-5269.

** N - New oil.

*** U - Used oil - J-57 engine test.

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